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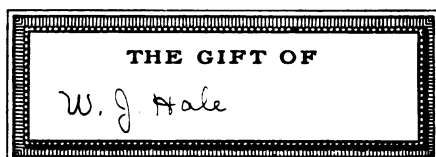
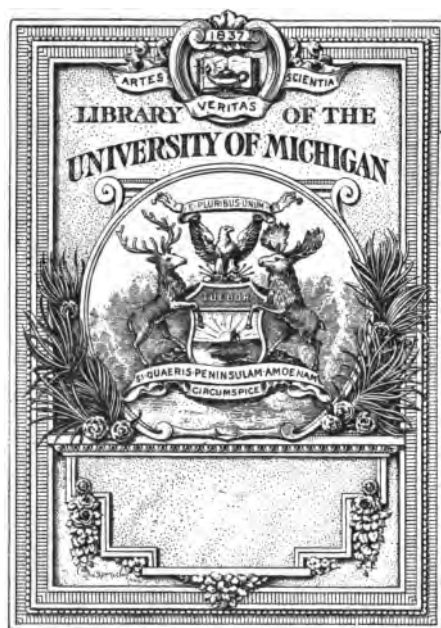
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Laboratory Outline *of* General Chemistry

FROM ELECTROLYTIC DISSOCIATION
TO THE METALS AND THEIR
COMPOUNDS



VOLUME II.

Privately Printed
ANN ARBOR, MICHIGAN
1907

*These experiments are taken primarily from
Prof. Alexander Smith's "Laboratory Outline
of General Chemistry" and all references
(marked with R) are made to his new book,
"Introduction to General Inorganic Chemistry."
— William J. Hale*

GEORGE A. SNYDER
Printer & Publisher
Dayton, Ohio

2500 M.F.

CHAPTER X.

IONIC CHEMICAL ACTIONS. INTERACTIONS OF ACIDS, BASES AND SALTS.

1. IONIZATION. How do we ascertain experimentally whether a substance is ionized in solution or not and learn the extent of the ionization [R. 310]? The degrees to which aqueous solutions of many substances are ionized are given in a table in the Appendix. Constant reference to this table will be necessary in interpreting the observations in this and succeeding chapters.

Obtain [Temp. order] a pair of electrolytic cells [Fig. 11], and observe that one cell is partially filled with dilute sulphuric acid. When the cells are connected in series with a battery, evolution of gas in this cell will indicate that the material placed in the second cell is a conductor, and that the circuit is therefore complete. If, on the other hand, the material in the second cell is a non-conductor, or at all events a very bad conductor, no evolution of gas will be observed in the first cell. When the substance placed in the second cell is a solution, what conclusion may be drawn in regard to the condition of the dissolved body? [R. 310].

Half fill the second cell with the substances named below in turn. See very particularly that the electrodes in each cell are on opposite sides of the glass partition, connect with the battery, and observe the effect in the first cell. When the same experiment has been shown in the lecture-room the result may be recorded here and the experiment omitted. Wash the cell and the electrodes carefully and dry well after each trial.

NOTE 14.—Nomenclature: In order that the nomenclature of the ions may be made as simple as possible, the following system has been adopted [R. 322]. The names of the cations are derived by adding the termination *-ion* to the stem of the element or radical, hydrogen, however, is called simply *hydrion*. When an element forms several ions of different valences, then the Greek prefix indicating the valence is applied. The anions derived from those substances whose names terminate in *-ous* or *-ite* receive instead the termination *-osion*, while those which originally terminated in *-ic* or *-ate* receive the termination *-anion*: the carbonate ion is usually shortened to *carbanion*. The elements or radicals retain in all cases whatever prefixes they originally had.

Solutions of ionogens in water are in fact mixtures of several physical components [R. 334] while in water alone there are three components, namely—the two ions and the undissociated

molecule (*water in equilibrium with hydron and hydroxidion*). The degree of this dissociation is found by conductivity determinations to be exceedingly small [R. 331], and hence the prevailing component is the undissociated molecule. In many cases the components theoretically possible can be present only to the slightest extent in a solution. Knowledge of these facts may be gained by reference to the dissociation table in the Appendix.

- a. Distilled water.
- b. Diluted aqueous solution of sodium hydroxide.
- c. Diluted aqueous solution of hydrochloric acid.
- d. Dry sodium chloride.
- e. Diluted aqueous solution of sodium chloride.
- f. Aqueous solution of sugar.
- g. Toluene.
- h. Solution of dry hydrogen chloride in toluene. [Obtain this from the side-shelf and return to the original bottle after the experiment].
- i. Concentrated acetic acid. [Obtain from side-shelf and return to the original bottle after the experiment].
- j. Diluted aqueous solution of acetic acid.

2. BASES AND ACIDS: PROPERTIES OF HYDROXIDION AND HYDRION.

a. Examine distilled water in respect to (a) taste, (b) behavior with litmus, (c) conductivity (cf. 1, a).

b. Examine toluene in respect to (a) behavior with litmus, (b) conductivity (cf. 1, g).

c. Examine an aqueous solution of hydrochloric acid in respect to (a) taste, (b) behavior with litmus (c) conductivity (cf. 1, c). (d) action on a piece of zinc, (e) action on a piece of marble. Acids in aqueous solution possess these properties in general. What ion common to all must then give these properties to their aqueous solutions? Express the components present in this solution in two sets.

d. Examine a sample of the solution of hydrogen chloride in toluene in respect to (a) conductivity (cf. 1, h), (b) action on a dried granule of zinc, and (c) action on a dried piece of marble. Be careful to use perfectly dry vessels in these experiments. What ion identified in c is here lacking? What difference in action has the water from that of toluene?

e. Dissolve a very small piece of sodium hydroxide in a test-tube full of water and examine the solution in respect to (a) taste, (b) behavior with litmus, and (c) conductivity (cf. 1, b). Bases are hydroxides of metals or metallic radicals and their aqueous solutions possess, to a greater or less extent, the properties just indicated. What component common to all must therefore have these properties? Write the five components present in a solution of sodium hydroxide in water.

f. The action of conc. sulphuric acid on zinc (Chap. IV. 2, d) and that of the dilute acid upon the same metal (Chap. IV., 2 c) indicated the difference in the properties of the two acids. Ascertain whether the action of (a) conc. acetic acid and (b) dilute acetic acid upon this metal, or any other metal e. g., magnesium, is in any way analogous thereto. To what inference does this lead in regard to the nature of the concentrated acid (cf. 1, i) and also of the dilute acid (cf. 1, j)? Why is the action so much more marked in the case of conc. and dilute sulphuric acid than with acetic acid. (See table in Appendix).

3. IONIC CHEMICAL CHANGES: I. NEUTRALIZATION. (Two students working together).

When solutions of two ionogens are mixed, a greater dilution for each ionogen results, but no appreciable change will be observed unless, by a crosswise combination between ions of opposite charge, the formation of a less ionized substance becomes possible [R. 337]. Pure water, for example, is only in the slightest degree ionized (cf. 1). If then a mixture of a solution of an ionogen supplying hydroxidions be made with one supplying hydriions, a most rapid and marked change would occur, whereby the slightly dissociated molecule—water—would form at the expense of these two classes of ions.

Dissolve about 5 g. of sodium hydroxide in 50 c.c. of distilled water and pour the clear solution into a burette. Mix in a small beaker about 10 c.c. of conc. hydrochloric acid with about 50 c.c. of distilled water and pour this into a second burette. Now, into a small beaker or flask run 15 c.c. of the acid solution from the second burette and then add to it two drops of phenolphthalein solution. Place the vessel under the first burette and run in the alkali very slowly at first and finally, when the color begins to spread throughout the liquid before vanishing, drop by drop, until the entire solution acquires the faintest perceptible pink tinge (with hydroxyl ions phenolphthalein gives a red color, with hydrogen ions it remains colorless). If the "end-point" (denoted by the appearance of the faint color tinge) is overstepped, then enough more of the acid solution must be added to bring back the faint tinge. The walls of the beaker or flask should always be washed down with distilled water before pronouncing the titration at an end (?). Concentrate the solution thus obtained on the sand-bath until a drop removed and cooled shows the appearance of crystals. At this stage promptly remove the dish from the sand-bath and set it aside. When a sufficient quantity of crystals have appeared, filter them off from the mother liquor and allow them to dry upon filter paper in a warm place. Examine them with respect to (a) form, (b) taste, (c) exposure to moist air, (d) action of a solution upon litmus and (e) conductivity of aqueous solution (cf. 1, e). Construct a table com-

paring the substance in these respects with the materials from which it was made. Compare the substance with common salt upon the side-shelf.

Draw up a table consisting on the one hand of the physical components present in the acid solution, and on the other hand of those in the alkaline solution. Ascertain, by reference to the dissociation table in the Appendix, the relative proportion in which these components are present in the above solutions, and again the tendencies those of opposite charges will have to form new substances (as inferred from the dissociation of these new substances that are less ionized). To what extent can these unions go [R. 339]? Why does the present reaction run to completion?

Express the change, here known as neutralization (why?), by means of symbols, using only the symbols that are concerned in this process. How may we define neutralization in terms of the ionic theory? What term is applied to the solid product obtained above as the result of neutralization?

NOTE 15.—From the theory of neutralization [R. 351] we observe that each and every hydron is removed by its union with an hydroxidion of a base. This gives us at once a simple means of determining the amount of base or acid present in an unknown solution, if we have at hand a solution of known concentration to titrate or balance against it. Standard solutions have been calculated on the basis of their containing but one hydrogen (1.01 g.) or one hydroxyl (17.01 g.) to the liter. Thus 40.06 g. of sodium hydroxide must be contained in one liter of its solution in order that the solution may be normal, *i. e.*, contain 17.01 g. hydroxyl. A solution of any fractional part of this weight to the liter would consequently be denoted by that same fraction of normality.

What was the (approximate) normality of the sodium hydroxide solution used in the above experiment? Calculate, from the ratio of the hydrochloric acid solution required for neutralization, the normality of the acid solution, and also the grams of hydrogen chloride present in a liter.

4. PARTIAL NEUTRALIZATION.

Fill a bottle with a potassium hydroxide solution (obtained from the side-shelf—the solution is about 5-normal). Slowly add, with constant stirring, about 15 c.c. of conc. sulphuric acid to about 35 c.c. of distilled water contained in a beaker surrounded with cold water. When the solution has reached the room temperature pour it into the second burette. Ascertain by titration as in 3 (q. v.) what volume of the alkaline solution will be required to exactly neutralize 5 c.c. of the acid solution. Pour the neutral solution thus obtained into an evaporating dish and concentrate it upon a sand-bath till its volume is about 10 c.c., then remove the dish from the bath and set aside to cool. Filter off the crystals that appear and dry them upon filter paper.

To a second portion of the acid solution twice the volume previously used (*i. e.*, 10 c.c.) add exactly the same volume of the alkali above used; now evaporate the solution to a volume of 5 or 6 c.c. and set aside to cool. Filter off the crystals formed and dry as before.

Compare the two lots of crystals as regards (a) form, (b) taste, (c) reaction of solution with litmus. Confirm by examining specimens of the same substances from the side-shelf.

From a study of sulphuric acid we observe that for its complete neutralization two hydrions must be removed from each molecule that goes into solution. Such was exemplified in the first titration above. In the second, however, the acid was double the amount that the measured quantity of alkali could neutralize, *i. e.*, the hydroxidions supplied could only remove one-half of the available hydrions, consequently the remaining portion of hydrions will be associated with the sulphurion as before. In other words we shall have a salt that possesses ionizable hydrogen formed by the partial neutralization of an acid *i. e.*, what is commonly called an "acid salt."

Express by an equation the first step of the dissociation of sulphuric acid in solution. Express also the dissociation of the "acid salt" in the process of its further neutralization by a base.

The molecular weight of sulphuric acid is 98. How many grams of pure acid would be contained in a liter of its normal solution?

5. IONIC CHEMICAL CHANGES. II. SALTS IN SOLUTION.

The application of the Law of Mass Action to ionic equilibrium.

a. The dissociation of salts in solution was demonstrated in the study of common salt (*cf.* 1, *d, e*). Are all salts in solution ionogens? From observations on the conductivities exhibited by conc. and dilute acids (*cf.* 1, *i, j*) what do you infer regarding the effect of increased dilution upon solutions of ionogens [R. 335]? How does the number of ions per unit volume, *i. e.*, the concentration, vary with dilution? On increasing the dilution of a solution of hydrochloric acid the increase in chloridions gives no color effect to the liquid which contains the colorless hydrions, and we therefore assume the chloridion also to be colorless. Examine a solution of sodium hydroxide or sodium chloride and determine whether the natrion imparts any color to its dilute solutions. Now take a minute amount of well-dried cupric chloride (about 0.2 g) in a dry test tube. Observe the color of the undissociated cupric chloride. Add 2 or 3 drops of water and shake. What color appears? Gradually add more water with constant shaking until all is dissolved. Continue in this wise until the change in color is complete. To what is the color due. Compare the color with that of a dilute solution and interpret the result (?) Should a conc. solution of sodium

chloride produce the same result as the hydrochloric acid? What effect has the increase in the concentration of the chloridions upon the cuprions present [R. 250]? Account for the variation in color between the dry salt and its diluted solution.

b. Fill a glass cylinder with water and into it pour one or two drops of a phenolphthalein solution, and then one drop of a solution of ammonium hydroxide. The red color at once developed indicates the presence of what ion? Now add to the solution in the cylinder some solid ammonium chloride (or a conc. solution of this salt) and notice the change (?) Explain the result. What became of the hydroxidions?

c. With a few exceptions (See Appendix) salts are all extensively ionized in dilute solutions. From our previous study we are led to believe that no decided chemical changes will be noticed, upon mixing solutions of salts, unless by a crosswise combination between ions of opposite charge a sparingly soluble (less ionized) molecule can be formed. Place 3 or 4 c.c. of a silver nitrate solution in a test-tube, dilute with water and then cautiously add a solution of potassium chloride until no further precipitation occurs. Filter off the precipitate, evaporate the filtrate to small bulk over a water-bath and pour it out upon a watch-glass to observe the formation of crystals (?) Write the reactions which indicate the ionization of the two salts and the formation of the final products from these ions. Is the formation of a precipitate theoretically essential in order that any change may take place between salts?

Will a solution of any soluble chloride produce the same result as above? Try solutions of hydrochloric acid, sodium chloride and calcium chloride respectively (?) What do these results show the solutions of these chlorides and potassium chloride to possess in common? From these data interpret the test for chlorides (cf. Chap. VII., 4; g).

Treat another portion of a dilute solution of silver nitrate with a few drops of a solution of potassium chlorate (?). What conclusion may we draw from this result in regard to the ions present in a solution of potassium chlorate? Does the complex ion *chloranion*, undergo further dissociation?

6. IONIC CHEMICAL CHANGES. III. DISPLACEMENT OF IONS.

a. THE HALOGENS. From observations already made compare the actions of the halogens upon solutions of their salts.

The action of free chlorine on the bromide ions (Chap. VIII., 2, c.)

The action of free chlorine on the iodide ions. (Chap. VIII., 6, d.)

The action of free bromine on the iodide ions. (Chap. VIII., 6, d.)

Relate to these the action of free fluorine on the salts of the

other haloids [R. 342]. The free element in displacing the combined element simply takes the electric charge of that combined element and enters itself into the ionic condition. This variation in power among the elements for displacing others from the ionic condition serves as a means of comparison, and a series so constructed as to show the gradual decrease in this power is known as an "electro-motive series." Arrange the halogens in the order of their tendencies to exist in the ionic state.

b. Action of Metals Upon Acids and Salts. The evolution of hydrogen by the action of metals upon acids may now be interpreted in terms of the ionic theory. In order, therefore, that zinc may replace hydrogen from an acid, we must assume that it possesses a greater tendency to exist in the ionic condition than does the hydrogen. Explain the action of zinc upon conc. and dilute sulphuric acid (cf. Chap. IV., 2, c, d. Chap. X., 2, f) on this principle.

What difference in action is observed when magnesium and zinc act upon an acid of the same strength? From the study of the elements with reference to this relative tendency to enter the "ionic condition" their order in an electro-motive series may be determined. [R. 362]. Any element above hydrogen will displace hydrogen from an acid and will likewise displace any succeeding metal from a solution of one of its salts.

CHAPTER XI.

SULPHUR AND ITS COMPOUNDS.

7. SULPHUR.

a. Place a small piece of roll-sulphur in a dry test-tube and add a few c.c. of carbon disulphide, shaking until sulphur is dissolved. Pour the clear solution upon a watch-glass and allow to stand for a short time (?). What is the form of the crystals?

b. Determine in a manner similar to that above the extent to which flowers of sulphur will dissolve in carbon disulphide.

c. Melt about 5 g. of roll-sulphur in a dry test-tube, applying the lowest temperature possible, and pour the molten mass into a beaker of cold water. Try the action of carbon disulphide upon the product and compare the result with that in a.

d. In a second test-tube gently heat about 5 g. of roll-sulphur until the boiling point is reached. Notice the changes in color and fluidity that occur (?). Pour the molten sulphur into a beaker of cold water and examine the product thus obtained as to its consistency and also as to its solubility in carbon disulphide (?). Set it aside for a few days and examine again in these respects.



e. Mix in a mortar $3\frac{1}{2}$ g. of iron filings and 2 g. of powdered sulphur. Transfer to a test-tube and heat gently. Observe the phenomena (?). When cool break the test-tube in a mortar and preserve the black product (?) for 8 a.

8. HYDROGEN SULPHIDE. [Hood].

a. Place a few grams of ferrous sulphide—or the product obtained in 7 e, in a test-tube and add a little dilute hydrochloric acid (?). Notice the odor of the gas evolved. Apply to the mouth of the tube a strip of filter paper moistened with a solution of lead nitrate [R. 705] (?).

b. Repeat the above experiment using conc. sulphuric acid in the cold and then in the warm (?). Try also the effect of dilute sulphuric acid upon the ferrous sulphide (?). How do you explain the difference in results? What physical component plays the important role in the dilute acid? What is the principal component in the conc. acid?

c. To a Kipp's generating apparatus for hydrogen sulphide or to the laboratory supply tap, attach by means of rubber tubing a small glass nozzle. Allow the hydrogen sulphide to flow out through the connections for a few seconds, or until the air has been sufficiently displaced, and then ignite the gas. What is the color of the flame? Hold a cold porcelain dish in this flame for a few minutes only and observe what substance is deposited on the plate by reason of its free existence in the interior portion of the burning gas. What other free substance may we infer to be present in the same region? What do these facts indicate regarding the stability of the gas at a moderately high temperature, and the difficulty therefore of synthesizing the compound by the direct union of its elements? What are the products of the complete combustion of the gas, and in what two stages does this combustion take place?

9. PROPERTIES OF HYDROGEN SULPHIDE IN AQUEOUS SOLUTION

a. Pass the gas into a test-tube one-half filled with distilled water until the solution smells strongly of the gas, *i. e.*, until the solution is saturated with it. Test the solution with litmus paper [R. 347] (?). Pour out a portion of it into a second test-tube and heat to boiling; test the solution again with litmus paper (?). What has become of the hydrions?

b. Allow the second portion of the above solution to stand for some time exposed to the air. Account for the appearance of the turbidity here acquired. Test for the presence of hydrions (?).

c. Prepare 10-15 c.c. of a saturated hydrogen sulphide solution, as just described in a, and add to the solution a few grams or iron dust. Allow to stand for a short time and notice odor (?). Filter off the insoluble matter and treat it in a small test-tube with dilute hydrochloric acid. Apply a strip of paper moistened



with lead nitrate solution to the mouth of the tube (?). What substance must have been present in the insoluble matter (cf. 8 *a*)? How do you account for the extreme slowness in the action of the iron [R, 374]?

d. Pass a vigorous stream of hydrogen sulphide through a few c.c. of an acidified potassium dichromate solution (cf. Note 13). Explain result, and account for the formation of the precipitate.

e. Pass a stream of the gas also through a small amount of an acidified potassium permanganate solution (cf. Note 13), and note results as in *d*.

f. Pass a stream of hydrogen sulphide through a few c.c. of water in a test-tube in which also a crystal of iodine has been dropped. Note what becomes of the iodine and further what substance is precipitated. What does the solution now contain?

What property of hydrogen sulphide do these last three experiments show?

From this tendency of iodine to take up the electric charge of the sulphur ions, what position in the electro-motive series would sulphur be given when considered along with the halogens (cf. 6 *a*)?

From 9 *b* the action of oxygen upon a hydrogen sulphide solution was observed. Relate to this the action of the halogens upon water (cf. Chap. VII., 2 *d*, Chap. VIII., 2 *a*, 6 *a*) and from these relations indicate the approximate position for oxygen when considered along with the "series" of the halogens and sulphur.

10. SOLUBLE SULPHIDES.

a. Place about 10 c.c. of a sodium hydroxide solution [Side-shelf] in a large test-tube and pass hydrogen sulphide into it until the point of saturation is reached (cf. 9 *a*). Test the solution with litmus paper and divide into three parts.

b. Add a little hydrochloric acid to one portion and test the escaping gases for the presence of hydrogen sulphide (cf. 8 *a*).

c. Into the test-tube containing the second portion add a pinch of powdered roll-sulphur, shake vigorously and let stand about 10 minutes. Notice the change in color. Filter the mixture and acidify the filtrate with dilute hydrochloric acid, testing the escaping gas as in *a* (?). What other product is here formed? What do these facts indicate in regard to the composition of the compound in the filtrate?

d. Allow the third portion from *a* to stand for a day or two and then acidify with hydrochloric acid (?). From the products thus identified what can you infer regarding the change which the original substance must have undergone? Give the cause of this change.

11. FORMATION OF A WEAK ACID—SULPHYDRIC ACID.

What do you infer from 9 *a*, *c* in regard to the concentration

of hydrions in a solution of hydrogen sulphide [R. 347, 374]? Write the components present in a solution of sodium sulphide and also in one of hydrochloric acid. When these two solutions are mixed what components (See dissociation table in appendix) would unite to form less ionized products and to what extent may these unions go? In the case of the formation of a volatile product, e. g. hydrogen sulphide, describe the disturbance of equilibrium and account for the great extent to which the reaction runs [R. 249]. Will a rise in temperature aid in this reaction? Why?

Define the term "weak acid." What are "strong acids?" By analogy how would you define a "strong base?" Relate the formation of a gas in a chemical reaction to that of a precipitate (cf. 5 c.).

12. HYDROLYSIS OF SALTS:—SULPHIDES.

Dissolve a crystal of sodium sulphide in water and ascertain what effect this solution has upon litmus paper.

NOTE 16.—As hydrogen sulphide in solution is a dibasic acid, it may form two classes of salts [R. 358], one of which may be expected to give an acid reaction and the other a neutral reaction to litmus. As a weak acid its dissociation into hydrion and hydrosulphidion is extremely small [R. 374], but the further dissociation of hydrosulphidion into hydrion and disulphidion is even less than that of pure water into hydrion and hydroxidion.

Write the components present in a solution of sodium sulphide. If now hydrosulphidion gives a smaller concentration of hydrogen ions than does water its formation will always be the more favored. From whence must the disulphidion obtain the hydrion that will transform it into hydrosulphidion? With the hydrions removed what ions will be left to give their characteristic reaction to the solution?

From these considerations what reaction to litmus may be expected of a solution that contains originally hydrosulphidions, e. g. a solution of sodium hydrogen sulphide (cf. 10 a) [R. 375]?

Define hydrolysis. What can you say in general regarding the salts of strong bases with weak acids, and vice versa?

13. INSOLUBLE SULPHIDES.

(Use of Hydrogen Sulphide in Analysis). Obtain from the side-shelf the following named solutions: Take but 2 or 3 c.c. of each, place in several test-tubes and dilute with about 20 c.c. of water. Pass hydrogen sulphide through the contents of each tube and observe the result.

- a. Copper sulphate.
- b. Cadmium sulphate.
- c. Lead acetate.
- d. Antimony trichloride.
- e. Zinc acetate.
- f. Manganese sulphate.

Add dilute hydrochloric acid to the contents of each tube and observe the effect. Only a small concentration of hydrions is thus seen to be sufficient to enable certain of the reactions above involved to proceed in the reverse direction. Filter off any particular one of the precipitates left unaffected by the hydrochloric acid and try the action of conc. nitric acid upon it (?). What is here found true of one is true for all the precipitates. Upon what does the reversibility of the above reactions depend? With this idea in mind classify in two groups the metals above named so as to indicate whether the formation of their sulphides is reversible with a small or with a high concentration of hydrions. Upon such principles as these are based the methods in use in Chemical Analysis.

14. SULPHUR DIOXIDE.

a. Touch a warm platinum wire to a bit of sulphur and bring the wire with the adhering sulphur again into the flame. Withdraw and notice the color of the flame from the burning sulphur and also the odor of the gas given off.

b. Heat in a hard glass test-tube a very small amount of iron pyrites. Observe the formation of a sublimate condensing upon the walls of the tube (?). What gas is evolved?

c. Fit up a flask (250 c.c.) as in Fig. 6 and attach to it, by rubber connections, an empty gas washing bottle which is to serve merely as a safety vessel. If experiment 15 is to be performed there should be attached a final second washing bottle, containing as a drying agent conc. sulphuric acid sufficient to cover the inlet tube about one-half inch. Into the flask place about 10 g. of copper turnings and admit 10 or 15 c.c. of conc. sulphuric acid. When the connections have been made air-tight heat the flask and its contents over a sand-bath and collect the gas as called for in experiments 15 and 16. Note the appearance of the contents of the flask as the action progresses.

d. Allow the flask with its contents, after the sulphur dioxide has been removed as in c, to stand over night. Examine the solid formed.

15. WEIGHT OF A LITER OF SULPHUR DIOXIDE [Quant. Hood].

Clean and dry a 250 c.c. flask and provide it with a tightly fitting cork. Weigh the flask and cork. This gives the weight of the flask filled with air. Now fill it completely with sulphur dioxide, by downward displacement of air, cork and weigh again. To insure its being full, repeat this operation till no increase in weight occurs. Finally, allow the gas to escape, and determine its volume by filling the flask with water up to the cork and weighing again. Observe the temperature and pressure of the atmosphere.

To obtain the weight of the empty flask and its cork, subtract

from the weight of the vessel filled with air the weight, under the observed conditions, of a volume of air equal to its content (1 liter pure dry air weighs 1.293 g. under normal conditions).

The difference between this corrected weight and that of the flask filled with sulphur dioxide is the weight of the latter. Reduce the volume of the gas to normal conditions and calculate the weight of 1 liter (?) and of 22.39 liters (?).

Enumerate carefully all the sources of error to which you would expect this way of determining the density of a gas to be liable. In doing this, consider each detail of the operation very critically.

16. PROPERTIES OF SULPHUROUS ACID.

a. Pass a stream of sulphur dioxide into a test tube full of water. Test the solution with litmus paper. What inference does this give regarding the compound present in an aqueous solution of the gas? Divide the solution into four parts for use in the following experiments.

b. Boil one portion of the above solution and then ascertain what action it exhibits with litmus paper. Does a solution of sulphur dioxide in water obey the law of Henry? From such data what may be inferred regarding the amount of sulphurous acid present in aqueous solution of the gas [R. 379]?

c. To the second portion of the acid solution add a solution of barium chloride (?) Remove a few c.c. of the mixture and add dilute hydrochloric acid to it. Identify the gas evolved (?) Is the action of barium chloride upon this acid solution reversible or not? Reserve the remaining portion for 19 c.

d. To the third portion add a few c.c. of hydrogen peroxide solution and reserve for 17 d.

e. To the last portion add a little bromine-water and reserve for 17 d.

f. Collect a bottle full of sulphur dioxide by downward displacement of air and place within the bottle some moistened litmus paper or grass (?).

g. Pass a stream of sulphur dioxide through an acidified solution of potassium dichromate (cf. Note 13) (?). Observe the changes.

h. Pass a stream of this gas also through an acidified solution of potassium permanganate (?). Observe the changes as in g.

17. SULPHURIC ACID. [Two students working together].

a. Obtain a distilling flask (100 c.c. capacity), a safety bottle with rubber connections (cf. 14 c), a wide-mouthed 1-liter bottle and a Chapman pump from the store-room. Fit up an apparatus as in Fig. 12. Charge the hard glass combustion tube with about 10 g. of pulverized iron pyrites, placing in the forward end of the tube a small loose plug of glass wool to prevent any sul-

phur from being carried over into the liter bottle. Now place in the distilling flask about 10 c.c. of pure conc. nitric acid. Finally connect the suction pump to the safety bottle, half filled with water, so as to indicate the rate at which air is being drawn through the apparatus. The total air admitted is easily regulated by the screw clamp between the pump and safety bottle, while the proportions passing through the combustion tube or through the nitric acid are regulated by the screw clamp at the end of the combustion tube.

First heat the pyrite in a very gentle stream of air until the sulphur burns. Then warm the nitric acid and divert part of the air current so that it may carry over a little of the vapor of the acid; heat the pyrite strongly and continuously. Repeat the introduction of air laden with nitric acid at intervals, by pinching the tube admitting air to the pyrite-burner, whenever the disappearance of the red fumes in the bottle shows that a further supply is needed.

After a crust of crystals (?) has formed in the bottle (there may be considerable delay before crystallization starts) remove the attachments and blow the gases from the interior by means of the bellows. If crystallization fails to begin after a reasonable time (note that an interaction even between molecules of gases may be slow, in spite of the completeness of the mixing), the cause is either the introduction of too much water along with the nitric acid, or the high temperature produced by chemical actions taking place in the bottle. Removing the attachments and cooling the bottle in a stream of water frequently brings it about.

Add 4—5 c.c. of water and wash down the crystals with it. Describe all that happens. If more of the product is required, the apparatus may be connected up again and a further supply of sulphur dioxide drawn into the bottle and subsequently more nitric acid vapor can be added. Finally any remaining crystals may be decomposed by water.

Filter the liquid in the bottle through a very small filter paper into a dish, rinsing the bottle with 2—3 c.c. of water, and evaporate on the sand bath [Hood] until the liquid begins to fume strongly (?). This will remove any nitric or nitrous acid that it may contain. Use the result for *b*.

b. Dilute the acid prepared in *a* with 2—3 times its volume of water. Dip a match stick into it and make marks on a sheet of paper. Set both paper and stick on radiator to dry (?).

c. Test the diluted solution with litmus and to a small portion of it add a solution of barium chloride. Observe the nature of the precipitate. Test its solubility in hydrochloric acid. This furnishes us with a distinctive test for the presence of sulphuric acid or soluble sulphates.

d. Add a solution of barium chloride to the solution obtained

in 16 *d, e* (?). What product is thus identified in the solution, and from its presence what is indicated regarding the tendency of sulphurous acid to undergo oxidation (cf. 16 *d, e*) ? Express the changes by equations.

18. REDUCTION OF SULPHURIC ACID.

a. Into a few c.c. of conc. sulphuric acid in a test-tube put a small piece of sulphur and heat to boiling. Notice the odor of the gas evolved (?). Account for its formation.

b. Repeat *a* substituting a small piece of charcoal for the sulphur (?). Recall the action of copper upon sulphuric acid in 14 *c*. What was the reducing agent in this latter case?

c. Pass a current of hydrogen sulphide through 2—3 c.c. of conc. sulphuric acid (?). What substances are here formed? Explain. Could conc. sulphuric acid be used to dry hydrogen sulphide?

19. SULPHITES.

a. To a solution of sodium sulphite add a little dilute mineral acid (?). What gas is evolved?

b. Add bromine-water to a solution of sodium sulphite, boil to expel excess of bromine and then add barium chloride solution to test for the presence of the sulphite ion.

c. Add bromine-water to the test-tube from 16 *c*. Test solubility of the precipitate in hydrochloric acid. Is this identical with that obtained in *b*?

d. Heat about 1 g. of sodium sulphite in a porcelain crucible over a blast-lamp. When cool acidify with hydrochloric acid (?). Identify the gas evolved. Account for the formation of any sulphur that may be precipitated.

20. THIOSULPHATES.

a. Dissolve about 5g. of sodium sulphite in about 20 c.c. of water. Add 4—5 g. of flowers of sulphur to the solution and boil for 10—15 minutes. Filter off the clear yellow solution and divide into two parts.

b. To one portion add a little dilute hydrochloric acid and observe results (often slow in coming). Compare with those obtained in 19 *a*.

c. Slowly pour the second portion of the solution into a test-tube containing a small amount of a solution of iodine in potassium iodide. What product is here formed? How might the "end-point" be ascertained? What distinction may here be drawn between the action of iodine and that of bromine or of chlorine upon sodium thiosulphate?

d. Heat about 1 g. of sodium thiosulphate very strongly in a porcelain crucible over a blast-lamp. Notice odor evolved. Identify the products liberated by acidification of the residue with dilute hydrochloric acid.

21. REDUCTION OF SULPHUR COMPOUNDS.

Take a pinch of any salt of a sulphur acid. Mix it with an equal quantity of sodium carbonate (anhydrous) and also with a like quantity of powdered charcoal, and heat the mixture strongly in a porcelain crucible (?). Place a portion of the mass upon a silver coin and moisten with one drop of water and then add a drop or two of dilute hydrochloric acid (?). This is known as the "hepar" test for sulphur in any form of its combinations.

CHAPTER XII.

NITROGEN AND ITS COMPOUNDS.

22. CONSTITUENTS OF THE ATMOSPHERE.

a. Proportion of Oxygen to Nitrogen by Volume [Quant.].

Fit a large test tube with a two-hole rubber stopper. Into one hole fit a short piece of glass tubing terminating in a nozzle and allowed to project but little beyond the bottom of the stopper. Into the other hole fit a short glass rod. Connect the glass tubing to a short-stemmed funnel by means of a rubber tubing (15 cm. in length) bearing a pinch clamp as shown in Fig. 13. The funnel may be advantageously supported by a clamp upon a retort stand.

Pour into the funnel an alkaline solution of pyrogallol prepared by mixing 3 c.c. of the pyrogallol solution with 20 c.c. of the conc. potassium hydroxide solution (both solutions obtained from the side-shelf and marked especially for this experiment.*

Now withdraw the glass rod from the rubber stopper and open the pinch clamp slightly so as to allow the alkaline solution to fill the rubber tube and nozzle completely. When the connections have been filled and the rubber stopper tightly fitted into the test-tube, replace the glass rod in the rubber stopper and thus enclose, under atmospheric pressure, a volume of air equal to the content of the test-tube. This operation should consume as little time as possible as the alkaline solution gradually absorbs oxygen from the air of the room and thereby becomes useless for further absorption.

The pinch clamp is now opened (care being taken not to warm the test-tube by handling), and a few drops of the alkaline solution allowed to enter the tube. As the oxygen is absorbed a vacuum is formed and more of the solution rushes in. Close the clamp and invert the test-tube, restore it to its original position

*_____

NOTE 17.—The two solutions are prepared so as to contain respectively, (a) 5 g. of pyrogallol dissolved in 15 c.c. of water (b) 120 g. of potassium hydroxide in 88 c.c. of water.

and again invert, thus bringing the liquid thoroughly in contact with the air enclosed. Finally, while in the inverted position, reopen the pinch clamp and equalize the level of the liquid in both tube and funnel. Close the clamp, restore the test-tube to its original position and mark the levels of the liquid and the bottom of the stopper, by means of rubber bands or paper labels.

Disconnect the test-tube—care being taken not to get the alkaline liquid on the hands—wash out the liquid and balance the dry test-tube in a beaker on a scale pan. Ascertain the volume of oxygen absorbed and the total volume of air in the tube by weighing the quantity of water necessary to fill the tube to the lower and upper marks respectively.

Calculate the percentage composition of oxygen in air by volume.

b. Place a few c.c. of a clear solution of barium hydroxide in a small beaker and allow to stand exposed to the air for several hours (?). The presence of what other substance has been identified in the air (cf. Chap. V, 3 b.) ?

c. Blow air from the lungs through a few c.c. of a clear barium hydroxide solution and compare with result in b.

23. NITROGEN.

a. Place about 10 g. of pure sodium nitrite and about 5 g. of ammonium chloride in a 250 c.c. flask fitted with a safety tube and delivery tube. Fig. 6.

If b is to be performed insert before the delivery tube a U-tube containing calcium chloride [Temp. order] for drying the gas.

Clamp the flask by the neck to a retort stand, add about 15 c.c. of water to it and warm gently [Caution]. As soon as the action begins remove the flame, bring a dish of cold water under the flask and cool it for a few seconds at a time so that the action may not become too violent but may run uniformly. After sufficient time has been allowed for the displacement of air from the apparatus, collect a bottleful of the gas over water in a pneumatic trough. Has the gas odor or color? Does it support combustion?

b. *Magnesium Nitride.* (Two students working together).

In a combustion tube place a porcelain boat one-half full of powdered magnesium. Connect one end of this tube to the outlet tube of the flask in a generating nitrogen. Bring a flame beneath the boat and heat the magnesium strongly (two Bunsen burners may be necessary). What action is noticed? What is the color of the product? Remove the boat and transfer its contents to a stoppered test-tube and reserve for 24 c. Will the same product be formed when magnesium is heated in the air? What other compound would be formed under the latter condition?

NITROGEN AND HYDROGEN.

24. AMMONIA [Hood].

a. In a small flask fitted with a one-hole stopper and delivery tube, place a mixture of about 10 g. each of powdered quicklime (calcium oxide) and ammonium chloride and heat gently (?). Collect a bottle of the gas by upward displacement. Does it support combustion? Note the odor of the gas [Caution].

b. Connect the delivery tube of the flask in *a* to the stem of a small funnel and bring the mouth of the funnel close to the surface of a small quantity of water held in a beaker (the funnel should not dip beneath the surface of the water (?). Preserve this solution, thus prepared, for 25. The evolution of ammonia by the action of strong bases upon ammonium salts serves as a test for the presence of the latter. How is the composition of ammonia by volume determined [Lect.]?

c. Boil the product from 23 *b* with a very little water in a test-tube. Do you obtain the odor of ammonia? Is this a general reaction for nitrides?

d. Heat a small piece of gelatine in a test tube and test the escaping gas for ammonia by its odor (?).

25. AMMONIUM HYDROXIDE AND AMMONIUM CHLORIDE—WEAK BASES.

a. What action has the solution from 24 *b* upon litmus paper? Is this a property possessed by dry ammonia [Lect.]? With what group of atoms are the hydroxidions here associated?

b. Pour a few c.c. of this solution into an evaporating dish and allow to stand exposed to the air for a day. Test again with litmus paper (?). Heat another portion in an evaporating dish for a few minutes and notice the odor from time to time [Hood]. What action will the final solution have upon litmus?

c. To a few c.c. of a solution of ammonium chloride in a test tube add a few drops of a sodium hydroxide solution (?). Notice the odor evolved.

Write the components present in the two solutions above and determine (See Appendix) which components, when the two solutions are mixed, will unite to form less dissociated bodies, and to what extent these unions can go.

Upon what does the completeness of the above reaction depend? Formulate the process by which ammonia is set free. Relate the results here to those in 24 *a*. Define "weak base" and illustrate (cf. 11).

d. Dip the end of a glass rod in hydrochloric acid and then bring this end over a solution of ammonium hydroxide. What is observed?

e. Neutralize the remaining portion of the solution of ammonium hydroxide from *a* with hydrochloric acid and evaporate to dryness over a water-bath. Compare the product with salt

used in 24 *a*. Place the substance in an evaporating dish and then invert over the salt and within the dish a small funnel (the stem of the funnel should previously be closed with a paper plug). Now heat the dish strongly over a flame and observe what product collects upon the side of the funnel (?). How could you apply tests to show that it is the same product as before (cf. 24 *b* and Chap. VII., 4 *g*)?

f. Place a few grams of ammonium chloride (or the product formed in *e* if sufficient in quantity) in the middle of an open-hard glass combustion tube. By means of a clamp upon a retort stand support this tube in a slightly inclined (5-degree) position. Put moistened pieces of red and also blue litmus paper in each end and heat the salt strongly (?). Watch very closely the effect upon each piece of test paper (?). What does this experiment indicate regarding the action of heat upon ammonium chloride? Which gas appeared first and which last, at the ends of the tube, and why first at both lower and upper ends? Has gravity any influence on the result?

NITROGEN AND OXYGEN.

26. NITRIC ACID [Hood].

Place about 10 g. of powdered sodium nitrate in a dry retort or distilling flask [Temp. order]. Cover the salt with conc. sulphuric acid and allow the acid to thoroughly moisten the entire mass. Selecting a small flask for the receiver bring the neck of it over the end of the exit tube of the distilling flask so as to avoid the escape of nitric fumes into the air of the laboratory. Partially surround this receiver with cold water or, what is better, wrap a damp cloth about it and keep the cloth moist with cold water. Heat the distilling flask gently and use the greatest care in handling the liquid distillate [Caution: *Serious wounds may be caused by the acid coming in contact with the skin*]. Reserve the sample for 31.

27. NITROUS OXIDE.

a. Cautiously heat 15–20 g. of ammonium nitrate [*Care*] in a flask provided with a one-hole stopper and delivery tube and collect three bottles of the gas over warm (?) water in a pneumatic trough.

b. Lower a glowing splinter into one of the jars thus collected. Does the gas support combustion?

c. Ignite a very small piece of red phosphorus in a deflagrating spoon and lower it into the second bottle of the gas (?). Compare the results obtained here and in *b* with those obtained in the case of oxygen. What change in volume, if any, will accompany this combustion? Express the volume relations by suitable formulæ.

d. Bring a bottle containing an equal volume of hydrogen, mouth to mouth with the third bottle of nitrous oxide. Allow a

few minutes for the gases to diffuse with one another, then separate the bottles by means of glass plates and, when ready, remove the plate from one jar and apply an ignited splinter. Compare the result with the combination of oxygen and hydrogen. What relation in volume will the gaseous products bear to the original constituents (a) at 100 degrees and (b) at room temperature? Express the reaction by an equation.

28. NITRIC OXIDE.

a. Into a small flask filled as in Fig. 6, and containing about 10 g. of copper turnings, pour 10—15 c.c. of water and then an equal amount of conc. nitric acid. Collect the gas evolved over water. Note the color of the gas first formed, and observe the color of the pure gas finally collected over the water. Fill two bottles with the gas and a third fill only one-half full, and allow it to remain in the trough for d.

b. Lower a glowing splinter into one bottle (?).

c. Lower a small piece of ignited red phosphorus, in a deflagrating spoon, into the second bottle (?). What volume change would result here? Compare the results in b and c with those under 27 b and c.

d. Into the third bottle from a, one-half full of the gas, slowly bubble oxygen enough to fill the bottle. Now carefully shake the bottle, keeping its mouth well immersed in the water, and observe result. How might the volume of oxygen in the air be determined by the use of this gas?

e. Prepare a few c.c. of a conc. solution of ferrous sulphate or ammonium ferrous sulphate (the latter keeps better for side-shelf use). Divide into two portions and into one pass a gentle stream of nitric oxide. Observe the color formed. What takes place on boiling the colored solution?

f. Dissolve about 1 g. of sodium nitrate in a few c.c. of water and add a portion of this 2—3 c.c. of the solution of ferrous sulphate from e. Pour conc. sulphuric acid cautiously down the side of the test tube so that it may form a distinct layer at the bottom. Notice a brown ring between the layers and explain by reference to e. *This constitutes a test for nitric acid or a nitrate.*

29. NITRIC PEROXIDE.

Heat 8—10 g. of dry powdered lead nitrate in a hard glass test-tube fitted with a one-hole stopper and delivery tube. Note the color of the gas given off (cf. 28 d.) Conduct the gas into a test-tube containing a strong solution of sodium hydroxide (prepared by dissolving 2 g. of sodium hydroxide in 7—10 c.c. of water). If a portion of the gas is not absorbed by the alkaline solution test the escaping gas for oxygen (?). What is the residue left in the hard glass tube after the gases have been completely driven off? Reserve the solution for 32 b.

30. Principles involved in making nitric acid.

a. From 28 *a* the action of copper on nitric acid was seen to give nitric acid, easily detected by its ready transformation into the red nitrogen dioxide. Is this a property of the acid alone, or will a solution of a nitrate act similarly? Try a solution of sodium nitrate upon copper (?).

b. Was nitric acid formed in 26 on mixing sodium nitrate and sulphuric acid before distillation began? Solve this question by mixing the materials (using finely powdered sodium nitrate), adding a very little water [Caution], agitating for a minute or two, and then applying the copper test as in *a*.

c. Test a mixture of phosphoric acid and sodium nitrate with copper as in *a* and ascertain whether this acid behaves as does sulphuric acid toward a nitrate. Could phosphoric acid be used in the preparation of nitric acid as in 26?

d. Is the action of sulphuric acid upon sodium nitrate reversible? Make a few c.c. of a conc. solution of sodium nitrate sulphate and add to it an equal or even greater volume of conc. nitric acid. Cool the mixture in a stream of cold water and stir with a glass rod (?). The salt solution must be sufficiently concentrated, otherwise the experiment will fail. Examine with a lens the crystalline product that separates out. What is formed? If the action is reversible what enabled us to obtain a large yield of nitric acid in 26?

31. PROPERTIES OF NITRIC ACID.

a. Use the sample from 26. Is its solution an acid? What is the color of the pure acid? What causes the yellow color?

b. Boil in a test tube [Hood] a pinch of sulphur with a few c.c. of pure conc. nitric acid (?). Dilute the solution with water and apply the test for sulphates. What property of nitric acid is here most prominent?

c. Dip a piece of wood into a few c.c. of nitric acid (?). The yellow color is due to xanthoproteic acid formed in this reaction.

d. The behavior of conc. and dilute sulphuric acid upon metals has already been studied. Try the action of both conc. and dilute (1 part acid to 10 of water) nitric acid upon (1) magnesium, (2) zinc, and (3) copper, and ascertain what gases are evolved in the several cases.

Place the metal, whose action is to be studied, in a test-tube fitted with a one-hole stopper and delivery tube and add the acid. Disregard the first portion of gas evolved, but as soon as the air in the apparatus has been displaced collect the gases in a test-tube over water in an evaporating dish.

The hydrogen set free will react with the acid under the several conditions and give various products. If the gases in the apparatus remain colored we may suppose nitric peroxide to be present. With the gases is the tube over water colorless but,

immediately upon exposure to air, turning to a red. we identify yet another gas. Nitrous oxide will support combustion while pure hydrogen may be identified by its inflammability. How may we identify the presence of hydrogen when it occurs along with nitric oxide? Where and in what condition will ammonia, formed by the complete reduction of the nitric acid, be found? How might its presence here be detected (cf. 25 c, d.)? The solution formed by the metal upon the acid should now be poured into an evaporating dish and evaporated to dryness [Hood] over a water-bath. Determine the nature of these products (?).

e. Try the action of tin upon conc. nitric acid (?). What evidence of action is there? When the action has exhausted itself add water and boil. Filter through a small filter paper in a funnel, wash the precipitate on the filter with water and observe whether the filtrate becomes neutral (?). Devise a way of ascertaining whether or not this solid remaining upon the filter is a nitrate (cf. 29)? What action of nitric acid is here observed?

f. *Aqua regia*. To 5 c.c. of nitric acid in a test tube add 10 c.c. of conc. hydrochloric acid. Warm [Hood] and notice the appearance and odor (?). When gold or platinum is placed in aqua regia they are dissolved as chlorides. Why will not dilute acids dissolve them (See table of solution tensions R. 362)? What becomes of the hydrogen ions in this aqua regia mixture? Could the active ingredient in this case be supplied as well under other conditions?

32. NITRATES AND NITRITES.

a. The action of heat upon ammonium nitrate and lead nitrate has been studied. The results with the latter is typical of nitrates of the heavy metals. The following typifies the behavior of nitrates of the alkali metals: Take a few grams of sodium nitrate and heat strongly in a hard glass test-tube till the evolution of gas has ceased (?). Test the escaping gas for oxygen. When the test-tube has cooled add a very few drops of water, and to one portion of the solution thus prepared add dilute sulphuric acid (?). Contrast the action here with that of dilute sulphuric acid upon a nitrate. Of the second portion of the above solution add a drop or two to some starch-potassium iodide emulsion and observe effect (?). Again add a drop or two of the solution to a few c.c. of a diluted potassium permanganate solution (?). These reactions serve for the detection of nitrates.

b. *Detection in the presence of each other*. Examine now the solution formed by passing the gases from heated lead nitrate into sodium hydroxide solution in 29. (1) for nitrites: Acidify a few c.c. of it with dilute sulphuric acid (cf. a). What gases are set free? Apply the other tests for nitrites as given in a above. (2) For nitrates: To the remainder of the alkaline solu-

tion, transferred to a small flask, add about 5 g. of ammonium chloride and heat to boiling. To what is the evolution of ammonia due? What other gas is evolved after the ammonia has been driven off? Test with a glowing splinter and compare with 23 *a*. The quantity of ammonium chloride added is much in excess of the required amount and thus complete decomposition of all the nitrite or unacted upon hydroxide is assured. When the action is over bring the emulsion into solution by the addition of sufficient water (about 10 c.c.) and then pour a few c.c. of the clear solution into a test-tube containing a few c.c. of a conc. solution of ferrous sulphate (cf. 28 *e*.) Carefully pour down the side of the test-tube conc. sulphuric acid and observe the test for nitrates.

CHAPTER XIII.

PHOSPHORUS.

33. When chlorine and oxygen are respectively allowed to act upon the allotropic modifications of phosphorus, what difference in behavior will be observed [R. 459]? What is the chief product formed when phosphorus burns in oxygen? What other product may be formed?

PHOSPHORUS AND HYDROGEN.

34. PHOSPHINE [Hood].

Place a very small piece of calcium phosphide in a little water in a beaker (?). Repeat using dilute hydrochloric acid instead of the water (?). Relate this action to those involved in the formation of ammonia and hydrogen sulphide, where other hydrides of non-metals are prepared from compounds of the non-metal with a metal. How may phosphine be freed from the impurity which it contains? Is pure phosphine spontaneously inflammable? In what ways does phosphine differ from ammonia?

OXYGEN COMPOUNDS OF PHOSPHORUS.

35. METAPHOSPHORIC ACID.

a. Drop a pinch of phosphorus pentoxide in minute portions at a time, into a test-tube containing about 10 c.c. of cold distilled water. What reaction takes place? Why could not the phosphorus oxide prepared by burning phosphorus under a bell-jar be used in this case? Test the solution with litmus paper and reserve for the following experiment.

b. To one portion of the above solution add a drop or two of silver nitrate solution and then add drop by drop a dilute solution of ammonium hydroxide (prepared by adding 1 vol. of ammonium hydroxide to 4 of water in a test-tube) until the precipitate formed remains permanent. Now add a few more drops of the ammonium hydroxide solution and ascertain whether the

precipitate is soluble in an excess of the reagent. If so, finally add a dilute nitric acid solution very carefully (just as with the addition of ammonium hydroxide) until the precipitate is reformed. Try the effect of a further addition of nitric acid. Do you find the precipitate soluble in this acid? What is the color of the precipitate in question?

c. In a small test-tube prepare a solution of egg albumen in water and to about 1 c.c. of this solution add a few drops of the acid solution from *a* (?).

d. The remaining portion of the acid solution from *a* should now be diluted with 5-10 c.c. of water and vigorously boiled in a test-tube for a half hour or more (a little more water may be required from time to time to prevent the contents of the tube going to dryness). Cool the solution and treat portions of it in the same manner as has been described under *b* and *c* above. What are the distinguishing characteristics between orthophosphoric acid as just prepared and the metaphosphoric acid in *a*?

36. ORTHOPHOSPHORIC ACID.

a. Heat about 1 g. of red phosphorus with 5-6 c.c. of dilute nitric acid in a test-tube [Hood] (?). When the action has ceased, filter, if necessary, and drive off the excess of water and nitric acid from the filtrate by evaporation over a water-bath [Hood]. Redissolve the syrupy residue in a little water, test with litmus paper and apply the tests given in 35 *b*, *c* and compare with the product studied in 35 *d*. What is the product thus identified? [A black precipitate, formed with the silver nitrate solution as in 35*b*, may here be obtained. It is due to the presence of phosphorous acid [R. 469] which acts as a reducing agent.

b. To a few c.c. of the solution from *a* add a few c.c. of a solution of ammonium molybdate in nitric acid [Side-shelf]. Warm the mixture gently but not to exceed a temperature of 60 degrees C. What is the product formed [R. 732]? This constitutes a delicate test for the presence of orthophosphoric acid. Might we expect to get this same precipitate from a solution containing metaphosphoric acid? Draw your reasons from the reaction studied in 35 *d*.

37. PHOSPHATES.

a. Strongly heat a few grams of dry sodium phosphate (the secondary sodium phosphate) in a crucible over a blast-lamp for 15-20 minutes, or until no further change in the mass is observed (?). When cold dissolve the mass in a little cold water and test a portion with a solution of silver nitrate (?). Acidify a second portion with acetic acid (?) and add a few c.c. of a solution of egg albumen to it. Compare these results with those obtained in 35 *b*, *c*, *d*, and 36 *b* for meta- and ortho-phosphoric acid. These reactions are those of pyrophosphoric acid.

b. Dissolve a small quantity of secondary sodium phosphate in water and ascertain its action upon litmus paper (?). Now add a solution of silver nitrate until the precipitation is complete (?). What salt of silver is here formed (cf. 35 d and 36 a)? If a tertiary silver orthophosphate is precipitated account for the available hydron of the original secondary sodium phosphate?

To answer this, test the filtrate from the silver precipitate with litmus paper or observe the action of the solution upon a few pieces of magnesium ribbon thrown into it (?). Why does not the available hydron of the secondary phosphate molecule show its characteristic reaction in solution [R. 466]? Are acid salts always acid toward litmus? If not explain why they are not.

c. To a few c.c. of a solution of secondary sodium phosphate add a few c.c. of "magnesia mixture." [This consists of a solution of magnesium sulphate to which first a little ammonium hydroxide and finally an excess of ammonium chloride has been added]. What is the precipitate formed? Observe the nature of this precipitate. *This serves as a test for the presence of phosphate ions.*

d. Strongly heat a few grams of microcosmic salt (sodium ammonium hydrogen phosphate) in a crucible over a blast-lamp until no further change takes place in the mass. What substances are given off in the form of vapor? Test the vapors with litmus paper. Dissolve the residue, when cold, in a little water and apply the tests as given in 35 b, c, d. [In applying the albumen test it will be necessary to make the solution acid with acetic acid as was done in 37 a.] The salt of what acid is then identified.

e. Make a bead of microcosmic salt by fusing a bit of it on the end of a platinum wire. Now fuse with it a single minute particle of cupric oxide (?). What is the color of the bead? Into what form of combination has the copper entered [R. 468]?

HALOGEN DERIVATIVES OF PHOSPHORUS.

38. TRIHALIDES.

The action of water on the tribromide of phosphorus has already been studied (cf. Chap. VIII., 3.)

a. Place about 2-3 c.c. of phosphorus trichloride in a test-tube and blow the breath over the mouth of the tube (?). Slowly add a little water, drop by drop (?). When about 5 c.c. of water have thus been added boil the solution. What is the gaseous product driven off in the vapor (test with litmus paper and with ammonium hydroxide upon a glass rod)? Remove a few drops of the solution in a separate test-tube and pass a current of hydrogen sulphide through it (?). How do you learn whether any reduction has taken place?

b. Now pour the remaining greater portion of the solution into an evaporating dish and evaporate to a syrup over a water-

bath [Hood]. Transfer a portion of this syrup to a small test-tube and heat over a flame until the gas passing off may be ignited at the mouth of the tube. Note the odor of the burning gas and thus identify it.

c. Test the product left in the test-tube, after the gas has been driven off, with a few drops of a solution of albumen. What acid are you able to identify? Write the reaction for its formation above. Test the second portion of the syrup from *b* with a dilute solution of iodine in potassium iodide (?). What acid is here shown to be present?

39. PENTAHALIDES.

Place a few small granules of phosphorus pentachloride upon a watch glass. Blow the breath over it. Carefully drop it into a few c.c. of water in a test-tube and boil (?). Evaporate the solution over a water-bath and apply the tests for the phosphoric acids as indicated in 35 *b, c, d*, 36 *a* and 37 *a*. Which acid is here detected? If any chloridions were present in the syrup (due to an incomplete evaporation) how might they be distinguished from the phosphanions?

CHAPTER XIV.

CARBON.

40. CHARCOAL.

a. Place a small piece of charcoal in a test-tube half full of water (?). Now sink it, if necessary, with copper wire and boil the water for several minutes (?). When the whole has cooled, test once more the tendency of the charcoal to float (?). Explain.

b. Boil dilute solutions of litmus and indigo, separately, with powdered animal charcoal and filter each liquid (?). The activity of the charcoal is much increased by previous heating in a covered crucible.

41. CARBON DIOXIDE.

a. Ignite a little charcoal in a crucible lid and place it under an inverted bottle. When the combustion is over (?) close the bottle by means of a glass plate and remove to the desk. Pour into it a few c.c. of lime water and shake. What is observed? Show that this same product results from the combustion of wood, paper, illuminating gas, etc.

b. Place a few small pieces of magnesite (magnesium carbonate) in a hard glass test-tube fitted with a cork and delivery tube and heat strongly. Allow the gas here evolved to bubble through a few c.c. of lime water in a test-tube (?). What is the residue in the hard glass tube [R. 643]?

c. Fit up a generating flask with a safety tube and connect

with two wash bottles containing water and concentrated sulphuric acid respectively (what is the use of each of these? The latter is unnecessary if 42 is omitted). Place in the flask some pieces of marble and pour upon them diluted hydrochloric acid. Collect two bottles of the gas by upward displacement of air.

d. Invert one bottle of the carbon dioxide from *c* over a vessel of water, and, keeping the mouth well immersed in the water agitate gently. Does the gas appear to be soluble in water?

e. In the second bottle insert a lighted splinter. Is the gas combustible? Does it support combustion?

f. Pass a current of the gas into a test-tube of distilled water. Test the solution with litmus (?). What is the action of the dry gas upon litmus? Boil the solution in a test-tube and test again with litmus (?). Explain.

g. Lead the gas into a little sodium hydroxide solution in a test-tube until the solution is saturated (test?). Let the solution evaporate spontaneously (first residue). Heat the dry residue (?) in a test-tube and determine what two things are given off.

To this residue after heating (second residue) add dilute hydrochloric acid until all action (?) ceases. Evaporate the solution on the water-bath and examine and taste this final residue (?).

Having recognized the products of the last action and taking into account the preceding observations, state what the nature of the second and first residues must have been. Write equations for all actions.

h. Pass a current of carbon dioxide into a solution of barium hydroxide (?). Filter off the precipitate and treat it with dilute hydrochloric acid in a test-tube (?). What is the test for carbonates? Is carbon dioxide exhaled from the lungs (cf. 22 *c*)?

i. In a hard glass test-tube, fitted with a cork and delivery tube, mix intimately 2 g. of powdered cupric oxide with 2 g. of powdered wood charcoal and heat [Blast-lamp]. Allow the gaseous product to flow into a second test-tube containing a few c.c. of lime water. The presence of what gas is detected? Treat the residue in the hard glass test-tube with a very little nitric acid (?). What is observed (cf. 28)? What is the reducing agent here?

42. MOLECULAR WEIGHT OF CARBON DIOXIDE [Quant.].

Determine the weight of 1 liter of the gas by the method used for sulphur dioxide (cf. 15), and calculate the weight of the gram-molecular volume at 0 deg. and 760 mm. What further information must we have to enable us to determine the formula?

43. CARBON MONOXIDE.

a. Heat about 10 g. of oxalic acid crystals with concentrated sulphuric acid in a generating flask with safety tube attached and fill a bottle with the gas which is given off. Shake with

lime water (?). With what substance should we wash the gas to remove the carbon dioxide? Arrange a wash bottle to purify the gas. Fill two bottles with the purified gas over water. Test one with lime water again (?). If the gas is pure, burn that in the other bottle, add lime water at once, close quickly and shake (?).

b. Devise a way of ascertaining roughly the relative volumes of the two gases generated in *a* and measure the proportion in a test tube full of mixed gases.

c. Pass a stream of the pure carbon monoxide over a little cupric oxide heated in a boat in a hard glass combustion tube. Describe what takes place and determine what gas is formed in this reaction. What is the reducing agent here?

CARBON AND HYDROGEN [HYDROCARBONS].

44. METHANE [Marsh Gas].

a. Powder about 5 g. of fused sodium acetate and about four times its weight of soda lime. Mix the ingredients intimately and place in a large test-tube fitted with a one-hole cork and delivery tube. Rap the test-tube gently so as to form a furrow along the upper surface of the mixture and thus allow for the passage of the gas. Then clamp the tube by its forward end in a slightly inclined (5 deg.) position so that it slopes toward this end (?). Slip over the tube a wire gauze (?), and, beginning at the rear or sealed end, heat the contents gently until the evolution of gas is uniform. When all the air is displaced collect two bottles of gas over water. Now attach a small nozzle to the end of the delivery tube and ignite the gas. Note the color and degree of luminosity of the flame (?). Hold over the jet a dry inverted test-tube and observe one product of the combustion (?).

b. Apply a flame to the mouth of one bottle of methane, with its mouth held downward (?). After the combustion pour into the bottle a few c.c. of lime water and shake (?). What product of combustion is hereby indicated? What volume of oxygen is required for the complete combustion of one volume of methane and what ratio will the resulting volume of gases bear to the original volume of methane?

c. Bring the second bottle of methane, with its glass cover, mouth to mouth with a bottle of chlorine which holds a volume of chlorine twice the volume of the methane. Now remove the glass plates from between the two bottles and allow the bottles to stand in this position for a few minutes. When the gases have become thoroughly intermingled (?) separate the bottles, closing each again with a glass plate. Allow one of the bottles to stand for an hour or more, care being taken that the glass plate cover has been previously well coated with vaseline to insure a good fitting and thus prevent any loss of gas by leakage. Apply a flame at once to the mouth of the second bottle and note

the result (?) Introduce moistened litmus paper (?). Is it bleached? Pour into the bottle a few c.c. of water and test the solution for hydrochloric acid (?). What other product resulted from this decomposition?

In the course of an hour apply a flame to the mouth of the second bottle (?). Introduce moistened litmus paper (?) and finally test the solution, made by shaking the contents of the bottle with a few c.c. of water, for the presence of hydrochloric acid (?). In what forms of combination is the carbon here found [R. 494]? Compare this result with that of the preceding case.

45. ETHYLENE [Hood].

Fit a 250 c.c. flask with a doubly bored cork, through which pass a safety tube and L tube, and connect with a wash bottle containing only a few drops of water (?). Place in the flask a mixture of 10 c.c. of alcohol with 25 c.c. of conc. sulphuric acid (this mixture should be carefully prepared beforehand). Heat the contents of the flask cautiously and collect, over water, a bottle of the gas that is evolved. Pass a slow stream of this gas through 1 c.c. of bromine covered with 5—6 c.c. of water (?) in a test tube. When the red color of the bromine has disappeared remove the layer of water from the lower oily layer by means of a pipette. Notice the odor of the liquid. Try its solubility in alcohol (?) Attach a nozzle to the delivery tube of the flask above and ignite the gas. Observe color and degree of luminosity of the flame (?).

Apply a flame to the bottle of gas above collected. Try tests to identify two products of the combustion (?).

Why is the accepted formula of the gas preferred to the simplest? What volume of oxygen is required for the complete combustion of one volume of ethylene and what will be the volume of the gaseous products?

46. ACETYLENE.

Fill a test-tube with water and invert it over a dish of water. Now place a small piece of calcium carbide under the mouth of the tube (?) and collect in the test-tube the gas evolved by the action of the water on this substance. Test the water in the dish with litmus paper (?). Compare this action with that of calcium phosphide on water in 34. Remove the test-tube from the dish and, noticing the odor of the gas, bring its mouth to a flame. Observe the color and degree of luminosity of the burning gas. Compare this flame with those of methane and ethylene (cf. 44 a, 45).

47. ILLUMINATING GAS.

a. Heat a small quantity of sawdust in a test-tube and notice

the odor of the escaping vapors (?). Test the vapors with blue litmus paper (?) and finally apply a flame to the mouth of the tube (?). What is the residue?

b. Repeat *a*, substituting a piece of bituminous coal for the sawdust (?).

c. *Reducing Action of Carbon and Certain Hydrocarbons in the Flame.* Heat the end of a platinum wire to redness and then dip it into a small quantity of pulverized potassium sulphate. Bring the adhering salt into the reducing portion of a slightly luminous Bunsen flame. After a few minutes remove the wire and molten salt. Place the bead upon a silver coin and moisten it with a drop of water or dilute hydrochloric acid (?). Explain the result (cf. 21).

48. ALCOHOL.

Dissolve 20 g. of molasses in 150 c.c. of water and add a little yeast. Fill a flask to the base of the neck with the mixture, plug the mouth loosely with cotton, and set the whole aside for 3—4 days. At the end of this time warm the solution and test the gas which is given off for carbon dioxide [R. 501].

Set up a condenser [Temp. order] and distilling flask (Fig. 16). Filter the liquid and distil off about 50 c.c., using an ordinary flask connected with the condenser by an L tube. Boil this portion in the distilling flask with a small flame and catch the part which passes over between 80 and 93 degrees.

Notice the odor of the distillate (?). Test its reaction with neutral litmus paper (?). Use one drop to ascertain whether it burns. To the rest add a crystal of iodine and enough sodium hydroxide solution to dissolve it. Shake vigorously and do not add more alkali than is absolutely necessary. Warm the solution and then cool it (?). This is the iodoform test.

49. ACIDS.

a. Add some dilute sulphuric acid to sodium acetate and warm. Notice the odor. How could you obtain acetic acid? How is it manufactured [R. 498] ?

Account for the ease with which this acid is liberated from its salts by dilute mineral acids (cf. 2 f).

b. Take some acetic acid and test its reaction with litmus (?). Recall its action on iron (cf. Chap. IV., 2 e). Add 1 g. of litharge (lead monoxide) to 2.5 c.c. of acetic acid and boil (?). Filter, if necessary, and set the clear solution aside to crystallize. Describe the product. What is its common name [R. 704].

50. ESTERS.

a. Place about 1 g. of sodium acetate in a test-tube, add 2-3 c.c. of alcohol and then finally a few drops of conc. sulphuric acid. Warm, if necessary, and notice the odor—characteristic of an ester. *This serves as a test for the presence of acetic acid or its salts.*

b. Place in a porcelain dish a piece of fat twice the size of a pea, and add 4 c.c. of alcohol and ten drops of 50 per cent. sodium hydroxide solution. Stir constantly and boil very gently until the odor of alcohol is no longer perceptible, then stop. The alcohol is used as a common solvent for the fat and the alkali. What is the residue. [R. 505].

Dissolve the soap in hot water, cool, and to half of the solution add dilute hydrochloric acid and shake vigorously (?). Withdraw the floating coagulum by means of a glass rod, suspend it in water in a test-tube, add a few drops of sodium hydroxide, and heat until solution takes place. What do you conclude from its solubility in alkali?

To the other half of the soap solution add calcium chloride solution (?). Explain the action of hard water [R. 506] on soap solution.

CHAPTER XV.

SILICON AND BORON.

51. SILICA.

Mix 1 g. of finely powdered silica with 4-5 g. of anhydrous sodium carbonate. Make a small watch-spring spiral on the end of the platinum wire [Instructions] and, by alternately heating in the Bunsen flame or blast-lamp, and dipping in the mixture, obtain a large bead and heat it strongly till all action (?) seems to have ceased. Place the bead in a test-tube and make others by the same process. Dissolve the beads in a small amount of water. Add hydrochloric acid a drop at a time until the solution is strongly acid (?). Evaporate the solution to dryness on the sand bath (?). Treat the residue with warm water, wash the whole contents of the dish into a test-tube and examine (?).

52. ANALYSIS OF A SILICATE.

Mix dry potassium carbonate with anhydrous sodium carbonate in equal proportions in a mortar. Coil the platinum wire to watch-spring form. Mix a little powdered talc (is this soluble in water? What is its common name?) with 6-7 times as much of the "fusion mixture" and hold some of the result on the platinum wire in the flame of the blast-lamp till it is completely melted and all action (?) has ceased. Repeat till several beads are obtained. Treat the beads with boiling water in a test-tube until they are completely disintegrated. Filter through a small filter paper and wash the precipitate with water. Preserve this filter paper and precipitate for use later. Acidify the filtrate with concentrated hydrochloric acid and proceed as in 51.

Make a hole in the paper and wash the precipitate obtained

above into a test-tube. Add dilute hydrochloric acid and warm (?). Filter, if necessary, and add ammonium hydroxide to alkaline reaction (?). The precipitate is aluminium hydroxide. Boil and filter. To the filtrate add a few drops of ammonium hydroxide, some ammonium chloride solution and some sodium phosphate solution and shake (?). Compare 37 c.

53. SILICON FLUORIDE.

Mix about 1 g. of calcium fluoride with an equal weight of sand, place in a test-tube and moisten the mixture with conc. sulphuric acid. Apply a gentle heat (?). Hold a glass rod, with a drop of water at its lower end, in the fumes of the gas (?). Account for the formation of the insoluble substance.

BORON.

54. BORIC ACID.

Make a strong solution of borax in boiling water in a test-tube. Add conc. hydrochloric acid until the solution is strongly acid and set aside to cool (?). Filter off the crystals, wash with a few drops of cold water, and dry by pressing between sheets of filter paper. Dissolve the crystals in the smallest possible amount of boiling water and set the solution aside. Filter, and wash the crystals as before.

Dissolve a part of the crystals in hot distilled water (neutral to litmus) and test the reaction of the solution to litmus paper (?). What conclusion do you draw in regard to the concentration of hydrions present in its aqueous solution? Dip a strip of turmeric paper in this solution of the acid, wrap it around the upper part of the test-tube and boil the solution until the paper becomes dry (?). Now touch the paper with a glass rod previously dipped in a sodium hydroxide solution (?). *This is a test for boric acid.* Treat the rest of the crystals with cold sodium hydroxide solution (?). Explain the formation of boric acid and its solubility in bases according to the ionic theory.

55. BORATES.

a. Dissolve some borax in distilled water. Test this solution and a sample of the distilled water simultaneously with neutral litmus paper, and, by comparing tints, determine whether the solution has any reaction (?).

Put two drops of the solution into a test-tube and dilute with water till the tube is two-thirds full. To the remainder add silver nitrate solution (?). Add silver nitrate solution to the very dilute solution also (?). The difference is more marked if the dilute solution is first warmed. For comparison, add silver nitrate solution to an exactly equally diluted sodium hydroxide solution (?). What conclusion do you draw in regard to the action of water on borax? Write the equation. Is the action reversible [R. 528]?

b. Dissolve a small crystal of borax in 1-2 c.c. of water in a

test-tube. Add a drop or two of sulphuric acid and then a few c.c. of alcohol. Heat the mixture and allow the vapors of alcohol escaping from the tube to catch fire (?). How is the flame colored? *This is a test for a borate.*

c. Heat a platinum wire in the Bunsen flame and while yet warm dip it into a small quantity of borax. Return the wire to the flame and observe the borax bead. Try the solvent power of this bead for various oxides e. g. copper oxide, manganese oxide, cobalt oxide and note the colors of the mixed metaborates formed [R. 528].

CHAPTER XVI.

METALS OF THE ALKALIES.

56. POTASSIUM HYDROXIDE.

a. Dissolve about 30 g. of potassium carbonate (what is the source of this salt?) in 200-300 c.c. of water in a large beaker and heat to boiling. Slake 15-20 g. of quicklime in a beaker (?), using heat if necessary to start the action, and make the product into a very thin paste with water. Add this gradually, and with constant stirring, to the boiling solution (?). Continue boiling for a few minutes. (Why are iron utensils exclusively employed in this operation when it is performed on a large scale [R. 553]?). Let the solution settle and, when it is cold, decant the clear liquid. Use the solution in *b* and *c*. Test the clear filtrate to ascertain if it contains any unchanged carbonate (?). How might this be removed?

What kind of hydroxides alone can be made by this method? Which hydroxides are of this kind [R. 553]?

b. ALKALIMETRY. Find the strength of this solution by titration. To do this, place a carefully measured volume (about 10 c.c.) of the clear solution in a small flask. Dilute with about four times its volume of water, as the concentrated solution is apt to decompose the indicator. Fill a burette with "normal" hydrochloric acid. Add some phenolphthalein solution to the alkali and run in the acid cautiously until the red color just disappears. Notice the volume of acid used. One liter of the acid contains 36.5 g. of hydrogen chloride.

Calculate the weight of potassium hydroxide per liter, which your measurement shows to be contained in the alkaline solution made in *a* (?). Express this also in terms of a normal solution containing 56 g. per liter (for example, 28 g. per liter would be .5 normal).

c. *Reactions of Hydroxyl Ions.* Note the slippery feel of the potassium hydroxide solution as above prepared (or as found

upon side-shelf). Place a few c.c. of a ferric chloride solution in a test-tube and add a little of this alkaline solution (?). What kind of hydroxides can be made by this method?

d. Expose a small piece of potassium hydroxide upon a watch glass to the air for a short time. Note the changes it undergoes (?). Acidify a portion of the product with dilute hydrochloric acid (?).

57. POTASSIUM NITRATE.

a. *Preparation of Potassium Nitrate.* Dissolve 25 g. of sodium nitrate and 22 g. of potassium chloride in 50 c.c. of water and evaporate to half the volume on the sand-bath. Decant the hot, clear liquid from the crystals and set it aside. Throw the crystals which appeared during boiling at once onto a filter and rapidly press out the rest of the mother liquor with a spatula. Examine the form of the crystals and ascertain what they are. (If they are too small, recrystallize a part slowly from water in a beaker in order to learn their form.) When the decanted liquid is cold, press the product on a filter likewise. Examine this set of crystals as before. Compare both with the original substances.

To understand the process study the solubilities of the substances concerned as they appear in the following table:

	Grams in 10 c.c. of water	
	10 degrees	100 degrees
Potassium nitrate	2.1	24.6
Sodium chloride	3.6	4.0
Potassium chloride	3.1	5.6
Sodium nitrate	8.1	18.0

Which of these substances will first be deposited from the boiling liquid? Ascertain by calculation how much of it (roughly) will be deposited at 100 degrees, how much more will come out when the liquid cools, and how much will remain in the mother liquor. What other substance will be present in large quantity in the hot mother liquor, and how much of it must there be? How much of this product will be deposited when the liquid cools, and how much will be lost by remaining dissolved? What per cent of the possible yield may we expect to get? Dry your product, weigh it and calculate what per cent was obtained.

Explain why purer potassium nitrate can be obtained by crystallizing the product once more from water.

b. Mix 5 g. of finely pulverized potassium nitrate with 2 g. of powdered charcoal and drop successively small portions of this mixture into a red hot crucible. Observe the action. What is the residue left in the crucible (test with an acid (?)) ? What gases were evolved in the reaction?

c. Repeat *b* above, using a mixture of 5 g. of finely pulverized potassium nitrate with 2 g. of sulphur (powdered separately (?)). What gases were evolved in the reaction? Test the residue, brought into solution with a little water, with a solution of barium chloride (?). Relate the results in *b* and *c* to the reactions that take place in the explosion of gunpowder.

58. POTASSIUM CYANIDE AND THIOCYANATE [Poison].

How is potassium cyanide made [R. 558]? Place 2 c.c. of potassium cyanide solution in an evaporating dish, heat it, and add yellow ammonium sulphide solution until the color no longer disappears. Evaporate to complete dryness [Hood]. Dissolve a part of the residue with water and add ferric chloride solution (?). A black precipitate (?) indicates that the heating was not sufficient. If this appears, heat the remainder once more and try the action of ferric chloride again. What property of the cyanides does the first part of this experiment illustrate [R. 508]. Show that the thiocyanate ion may serve as a delicate test for the presence of the ferric ion. To what component is the red color due? What would be the action of potassium chloride upon the red solution [R. 250]?

59. REACTION OF POTASSIUM SALTS.

a. Heat a little solid potassium nitrate on a clean platinum wire. Notice the color of the flame and examine with the spectroscope. Make a diagram showing the position of the lines with reference to the D line, which, on account of the sodium present, is shown by all flames in the laboratory.

b. Dissolve as much potassium nitrate in 10 c.c. of water as gentle warming will allow. To this concentrated solution add about an equal volume of a strong solution of tartaric acid. Shake the mixture and cool in a stream of water (?). Note, also, the effect of rubbing the inside of the test-tube with a glass rod. Describe the product. Filter, press out the mother liquor, and wash the precipitate with a little alcohol. Dry by pressing between filter papers. The nature of the product (?) may be inferred from the results of *c* and *d*.

c. Dissolve a little of the precipitate in warm water and test its reaction with litmus paper. Test the solubility of the precipitate in hydrochloric acid and also in potassium hydroxide solution (?).

d. Place half the remainder in a test-tube and add sodium carbonate solution a drop at a time, mixing thoroughly, and noticing all that happens (?). If any change is observed, let the action go on until it is complete. Can you explain why evidence of the beginning of the action is so slow in making its appearance?

Add concentrated hydrochloric acid, a drop at a time, to the resulting solution (?). Stir vigorously with a glass rod at inter-

vals. Finally try the effect of an excess of hydrochloric acid (?).

e. Heat the rest of the precipitate strongly in a porcelain crucible (?). Extract with hot water, filter, and add any acid to the filtrate (?). The ignition of all potassium or sodium salts of organic acids gives the same result.

f. To potassium chloride solution, add picric acid solution (?).

What is shown to be present in a solution when we get the tests in *b* and *f*.

60. SODIUM.

Recall the properties of the metal as you have met them in previous exercises. Expose a small piece of sodium hydroxide upon a watch glass to the air and ascertain what takes place. Relate these changes to those observed in 56 *d*.

61. PREPARATION OF SODIUM CARBONATE BY THE SOLVAY PROCESS.

Take 75 c.c. of ammonium hydroxide solution, diluted with 25 c.c. of water, dissolve in it 25 g. of powdered ammonium carbonate by shaking, and then saturate the solution completely with sodium chloride by prolonged agitation with finely powdered salt in a corked bottle. If common salt is employed, it should be washed with water before use. Decant the clear liquid into another bottle, fitted with cork and two tubes, one of which reaches to the bottom. Through the latter, pass in carbon dioxide from a Kipp's apparatus until the solution is saturated. This operation may occupy an hour or more. During the absorption of the carbon dioxide, the exit tube should be closed to prevent waste of the gas. Close the tubes with caps of rubber tubing plugged with glass rods [Instructions] and set aside over night (?). Filter off the deposit and dry by pressing between filter papers.

Dissolve in water a little of the solid, which must have ceased to smell of ammonia, and test the reaction of the solution with litmus (?).

To part of the solid add dilute mineral acid (?).

Heat the rest in a test-tube clamped so that the mouth is inclined slightly downward, and ascertain what gases are evolved. When gas ceases to be given off, dissolve the cold residue in a very little water, test the reaction of the solution with litmus paper (?), and set it aside to crystallize in an open dish (?). Ascertain the effect of exposure in an open vessel (?) and the action of acids (?) on the crystals.

The solubilities at 20 degrees of the bicarbonate and carbonate in 100 parts of water are 9.6 and 92.8 respectively. Explain why the bicarbonate is made first and then the carbonate from it.

62. PREPARATION OF SODIUM ACID CARBONATE FROM THE CARBONATE.

Prepare a concentrated solution of sodium carbonate in about 10 c.c. of water and pass a stream of carbon dioxide into the

solution until a copious white precipitate is formed (?). Filter off the crystalline mass. Dissolve a little of it in water and test the solution with litmus paper (?). Finally heat the remainder and ascertain what gas is given off (?). Relate this experiment to 61. Is this a general reaction for acid carbonates? Write the reactions involved in the two stages.

Is the action of sulphur dioxide upon a solution of sodium sulphide analogous to this? If so, write the reactions corresponding to those involved here.

63. PURIFICATION OF SODIUM CHLORIDE.

Wash some crude salt with water and then prepare about 150 c.c. of a cold saturated solution by grinding the salt for some time in a mortar with the water. Place it in a beaker and pass hydrogen chloride into the solution. Prepare this gas by placing a concentrated hydrochloric acid and allowing concentrated sulphuric acid to fall into it from a dropping-funnel. Deliver the gas into the solution through a thistle tube with the mouth downwards (why use this tube?) When considerable precipitation has occurred, filter by putting a clean silver coin in a funnel, pouring the liquid and crystals upon it and pressing with a spatula.

Explain why the salt is precipitated. If sodium sulphate or magnesium chloride or some other salt has been mixed with the salt, would they have been thrown down [R. 584]? In other words, why does this process give a means of purification?

Explain the method of generating hydrogen chloride used above.

This question may be answered after the experiments in 64.

64. IONIC EQUILIBRIUM.

a. Dilute a few drops of methyl orange solution with distilled water. Add to it first a few drops of an acid (?) and then a few drops of a base (?).

Take four portions of distilled water and add to each a little methyl orange solution. To the first two add a little acetic acid (?), to the last two a drop of hydrochloric acid (?). What kind of ions is absent when the indicator is yellow? Add some solid sodium chloride to the first and stir (?). To the second add solid sodium acetate and stir (?). Explain the difference in behavior. To the third add solid sodium chloride and stir (?). Explain absence of effect. To the fourth add solid sodium acetate and stir (?). Explain.

b. Take three portions of a saturated solution of potassium chlorate in as many test-tubes. (This and the following solutions must be shaken to insure saturation if there is a deposit in the bottles.) To the first add saturated sodium chloride solution (?), to the second saturated potassium chloride solution (?), to the third saturated sodium chlorate solution (?). Allow them to

stand for a minute or two before drawing any conclusion. Explain. The experiments will fail if the solutions are not saturated.

65. REACTIONS OF SODIUM SALTS.

Use a solution of sodium chloride.

a. Dip a platinum wire into the solution and hold it in a non-luminous flame (?). Examine the sodium flame by means of a spectroscope. Compare with potassium spectrum.

b. To the salt solution add a picric acid solution (?). Compare with that obtained with potassium salts (cf. 59 f).

c. Try the effect of adding a solution of tartaric acid to a concentrated salt solution (?).

66. AMMONIUM SALTS.

a. What is the effect of heating ammonium salts (cf. 25 f)? Heat some ammonium phosphate in a hard glass test-tube (?). Dissolve the residue in water and test with litmus paper. Heating and searching for an odor of ammonia is not a sure test for ammonium salts. In many cases the odor would not be perceived.

b. Does an ammonium salt impart a color to the flame?

c. Add a picric acid solution to a solution of an ammonium salt (?). Compare with the results under potassium and sodium.

d. Add an excess of a tartaric acid solution to a solution of an ammonium salt (?). Compare with results obtained with potassium and sodium salts.

e. To another portion of a solution of an ammonium salt add a sodium hydroxide solution (?). Note the odor. Will all ammonium salts react similarly with strong bases? Which are our strongest bases? How could you detect the presence of ammonium, sodium or potassium in mixtures containing all three?

Make a list of the salts of potassium, sodium, and ammonium which are least soluble.

CHAPTER XVII.

METALS OF THE ALKALINE EARTHS.

67. CALCIUM OXIDE.

Ignite 2—3 g. of finely powdered marble in an open porcelain crucible, for about 15 minutes, at the highest temperature of the blast-lamp (?). Stir the mass occasionally with a glass rod or platinum wire. When cool add a little water to the product (?) in the crucible. What do you observe? Test the reaction of the liquid toward litmus (?). Has water any effect upon marble? now try the effect of adding a little dilute hydrochloric acid to the contents of the crucible (?). Compare this with action of the acid upon marble (cf. 41 c). What was formed by the ignition of marble? As the action is reversible what precautions must be

observed to insure the complete decomposition of the marble? On what will the re-formation of marble at any given temperature depend [R. 591]?

68. CALCIUM HYDROXIDE [LIME WATER].

Slake a small piece of calcium oxide and shake the product with half a liter of distilled water, let the solution settle, and use the clear liquid.

a. Blow air from the lungs by means of a tube through a part of the lime water (?). How could you determine the proportion of carbon dioxide in a sample of air?

b. Pass a persistent stream of carbon dioxide, from a Kipp's apparatus, through the remainder of the lime water (?). Boil a part of the resulting clear solution (?). Explain [R. 594].

69. REACTIONS OF CALCIUM SALTS.

Dissolve about 2 g. of calcium chloride in 100 c.c. of water and use the solution for the following experiments. [In all paragraphs headed "reactions," where diluted solutions are called for, the strong solutions on the side-shelf must be diluted with three to four times their volume of water to secure good results].

a. Try the flame test and examine with the spectroscope (see that the platinum wire is clean). Make a sketch of the spectrum showing the positions of the lines with reference to the sodium and potassium lines.

b. To a small portion of this solution add a little ammonium oxalate solution (?). [The formation of all precipitates, if long delayed, may be hastened by vigorous stirring with a glass rod]. Filter off the precipitate and divide into two portions. Treat one in a test-tube with hydrochloric acid (?) and the second portion in another test-tube with acetic acid (?). How do you explain this difference in action toward the hydrogen ions [R. 598]? Why was a salt of oxalic acid used above in preference to the free acid?

c. To a second portion of the calcium chloride solution add a solution of ammonium carbonate in excess (?). Warm if necessary. Filter the contents of the tube, and to the clear filtrate add a solution of ammonium oxalate. Do you notice a precipitate? Even if only a slight turbidity is observed how would you rate the comparative insolubility of the precipitate here with that in *b*?

Try the action of hydrochloric acid (?) and also that of acetic acid (?) upon portions of the precipitate obtained above. Relate this to the action of these acids upon calcium oxalate (cf. *b*).

d. Repeat experiment *c* but this time boil for about 15 minutes (?). Do you obtain a precipitate? If not, account for the difference in action. Test the issuing vapors with litmus paper (?). Test the clear liquid with a little ammonium oxalate solution (?).

e. Action of the Acid Carbonate Ion Upon Calcium Salts.

To a third portion of the calcium chloride solution add a solution of sodium acid carbonate (?). Filter the contents of the tube and divide the filtrate into two portions. Add a little ammonium oxalate solution to one of these portions (?). Boil the second portion (cf. 68 *b*), filter off the precipitate (?) and test the filtrate with ammonium oxalate solution (?). How may the normal carbonate as prepared in *c* be converted into the acid carbonate in solution (cf. 68 *b*) (cf. 62)? This acid carbonate gives to water its temporary hardness. Why called "temporary"?

f. Add to a fourth portion of the calcium chloride solution an excess of dilute sulphuric acid (?). Filter and divide the filtrate into three portions. To one small portion add an equal volume of alcohol (?). How does this affect the solubility of calcium sulphate? To the second portion add sufficient ammonium hydroxide to neutralize any acid present and then a solution of ammonium oxalate (?). What can you say of the amount of calcium sulphate that may be dissolved in water? Compare this with the amount of calcium carbonate (cf. *c*) and acid carbonate (cf. *e*) that may dissolve in an equal volume of water.

Calcium sulphate gives to water its permanent hardness. Boil the third portion of the filtrate above. Can permanent hardness be removed by boiling? Add now a little sodium carbonate solution (?). Compare the solubility of the sulphate with that of the carbonate.

70. REACTIONS OF STRONTIUM SALTS.

Use a strontium chloride solution containing 0.5 g. of strontium chloride to 50 c.c. of water.

a. Try the flame test and observe with a spectroscope.

b. Add a little ammonium oxalate solution to a portion of the strontium chloride solution (cf. 69 *b*) (?).

c. Add ammonium hydroxide and ammonium carbonate to another portion of the solution (?).

d. To a third portion of the solution add a few c.c. of dilute sulphuric acid (?).

e. In order to determine the relative solubility of calcium and strontium sulphates make a solution of calcium sulphate by shaking a little of the powdered salt with water and decanting off the clear liquid. Pour some of this liquid into a portion of the strontium chloride solution and explain. The precipitate may take place very slowly.

71. REACTIONS OF BARIUM SALTS.

Use a diluted solution of barium chloride.

a. Try the flame test and examine with the spectroscope.

b, c. Same as in 70 *b, c.*

d. To a portion of the barium chloride solution add a few c.c. of dilute sulphuric acid (?).

e. In order to determine the relative solubility of the sulphate of barium and strontium make a solution of strontium sulphate by shaking a little of this salt with distilled water and decanting off the clear liquid. Add a few c.c. of this strontium sulphate solution to one of barium chloride and explain. Relate the result here to that obtained in 70 e, and from these data arrange the sulphates of these three elements in the order of their solubility in water. How could you tell a solution containing the ions of a member of this family from one containing those of the previous family?

Give two methods of distinguishing between the members of the present group.

b. Add a solution of potassium dichromate to a little barium chloride solution (?). Try solubility of precipitate in hydrochloric acid (?) and also in acetic acid (?).

72. Apply to the instructor for three unknown substances, and ascertain what each is, testing first for the bases and then for the acids present. Follow the line of work outlined in the Appendix.

CHAPTER XVIII.

COPPER AND SILVER.

73. CUPROUS CHLORIDE.

a. Dissolve about 1 g. of cupric chloride in 10-12 c.c. of water in a test-tube. Drop in some copper turnings and boil rapidly till the change in color is complete or until the green tint is no longer perceptible in the dirty yellowish-brown color of the product (?). If a few drops added to a test-tube full of water confer a blue tinge (?) to the water the action is still incomplete. When the blue color no longer appears what ion is proved to be absent (cf. 5 a)? What is the color of the cuprous ion?

What effect has the molecular copper upon the doubly charged positive cupric ion [R. 620]? What charge does the cuprous ion carry? Is this a process of oxidation or reduction? Explain.

b. To a small portion of the above solution, when cold, add a sodium hydroxide solution (?). Divide the mixture into two parts. Shake the test-tube containing one part with as much air as possible and observe whether the precipitate undergoes any change (?). Heat the other part (?). Relate this to the action of sodium hydroxide upon copper sulphate (77).

c. Pour a portion of the cuprous chloride solution into a large amount of water in a beaker (?). Expose some of the product, while covered with water, to the sunlight (?).

d. Into the test-tube containing the cuprous chloride solution, together with some of the salt that separates out on cooling, pour

a little dilute hydrochloric acid (?). Do you find this salt to be readily soluble in the acid? What is formed by this solution [R. 620]? Pour a little of the clear solution into some water (?). Does it still give the precipitate as observed in *c*? Add now a few drops of nitric acid to this hydrochloric acid solution and notice the change in color (?). To what is this due? Pour the solution into water. Do you observe a precipitate? Account for the difference in action here from that in *c*. What role did the nitric acid play? The increase in negative chlorine ions taken up is explained by what change in the charge of the cuprous ions (cf. *a*)? Upon this basis how may we define oxidation?

e. What is the complex negative ion formed when cuprous chloride is dissolved in hydrochloric acid [R. 621]? Does this complex negative ion give a smaller or greater concentration of cuprous ions than the insoluble cuprous chloride? Upon this basis explain the solubility of cuprous chloride above.

74. CUPROUS IODIDE.

To a dilute solution of copper sulphate add a solution of potassium iodide. Note the color of the precipitate (?). How do you account for the color of the solution? Filter off the precipitate and test a portion of the solution with a starch emulsion (?). Test a second portion by shaking it up with a little chloroform (?). What can you say of the stability of a 'cupric iodide' [R. 621]? Is cuprous iodide affected by light?

75. CUPROUS CYANIDE.

Add a solution of potassium cyanide drop by drop, to a solution of copper sulphate (?). What is precipitated? Now add an excess of the reagent—potassium cyanide—till the precipitate is redissolved. In what form of combination is the copper [R. 624]? What can you say of the ionization of the cuprocyanidion as compared with that of other copper compounds [R. 624]? From this fact will potassium cyanide dissolve other insoluble copper salts? Reserve the solution for this investigation in 79 *b*, *c*.

76. DOUBLE SALTS.

Saturate water at 70 degrees with 5 g. of finely powdered potassium sulphate (about 25 c.c. will be required). Calculate the weight of crystallized cupric sulphate which must be taken to get an equi-molecular proportion, and dissolve it in its own weight of hot water. Mix the two solutions, taking care not to allow any undissolved fragments of either salt to get into the mixture, and set the result aside to crystallize (?). Examine the form of the crystals and compare with those of blue vitriol (?). Reserve for use in 79 *b*.

77. CUPRIC HYDROXIDE.

a. Add a solution of sodium hydroxide to a solution of copper sulphate (?). Filter off the precipitate and divide into two portions.

b. Boil one portion with water in a test-tube (?). What change is produced [R. 623]?

c. To the second portion, covered with water in a test-tube, add a little glucose (or cane sugar in water boiled with a few drops of dilute sulphuric acid). Warm gently (?). What is the product thus formed? Will cupric hydroxide be precipitated by sodium hydroxide in the presence of reducing agents? This reaction may serve also as a test for glucose [R. 623].

78. CUPRAMMONIUM SALTS.

To a solution of copper sulphate add at first a very few drops of ammonium hydroxide (?). What is the substance thrown down [R. 625]? Compare with the action of sodium hydroxide upon a cupric salt (cf. 77 a). Now add an excess of ammonium hydroxide (?). To what is the color due [R. 625]? Reserve the solution for 79 b, c. Do other salts of copper behave in a similar manner towards ammonium hydroxide? Try, for example, a solution of copper nitrate (?).

Now try the solubility of cuprous chloride (from side-shelf or from 73 a) in ammonium hydroxide (?). What is the color of the solution? What complex ion is formed? Does this complex ion give a less concentration of copper ions than does the insoluble cuprous chloride [R. 622]? Does this ion readily take on an increase in positive charge? Shake the solution with a large access of air (?) and ascertain what ion is now present. Does the blue complex ion give a less concentration of copper ions than many copper compounds e. g. copper hydroxide (for the sulphide cf. 79 b)? What can you say of the use of ammonium hydroxide as a test for the presence of copper?

79. REACTIONS OF CUPRIC SALTS.

Use a diluted copper sulphate solution. What is the color of the copper sulphate itself? To what is the color of the solution due?

a. Test the reaction of the solution toward litmus paper (?). Does this point to copper as a strong base?

b. Pass hydrogen sulphide through a portion of the copper sulphate solution (?). Filter off the precipitate and try its solubility in (1) hydrochloric acid, (2) boiling dilute nitric acid, (3) ammonium hydroxide, (4) potassium cyanide solution.

May we expect copper sulphide to be precipitated from a solution acidified with hydrochloric acid?

From the action of ammonium hydroxide above may we expect copper sulphide to be precipitated from a solution containing cuprammonium ions? Confirm by passing hydrogen sulphide through a portion of the solution from 78 or any ammoniacal copper solution (?).

From the action of potassium cyanide what are we to infer

in regard to the effect hydrogen sulphide will have upon a solution containing cuprocyanide ions? Confirm by passing the gas through a portion of the solution from 75 (?).

Dissolve some of the crystals from 76 in water and apply the test with hydrogen sulphide (?). How may we distinguish between a double salt as in this instance and a salt of a complex ion as potassium cuprocyanide?

c. Add a solution of potassium ferrocyanide to a little copper sulphate solution (?). Is this a delicate test? Will this reagent precipitate the same brown compound from solutions which contain the copper in the form of complex ions? Try the action of this reagent upon the last portion of the cyanide solution from 75 (?). Try also its action upon a solution of copper ammonium sulphate (from 78) (?). What determines whether the precipitate will form in these cases? How does this reagent act upon a solution of the double salt from 76? Explain.

d. Make a borax bead (cf. 55 c) and heat it with a minute particle of cupric oxide in the oxidizing (?) and in the reducing (?) flame. The latter requires patience.

e. Slightly char the end of a match, or better, a somewhat larger splinter of pine wood, and rub the charred part with a heated crystal of sodium carbonate [Instructions]. Place on the end a moistened mixture of any copper salt with anhydrous sodium carbonate and heat in the reducing region of a small Bunsen flame. Break up the charred stick gently in water in a mortar, wash away the lighter particles, and examine the residue.

80. Into a solution of copper sulphate, in a small evaporating dish, drop a fragment or two of zinc. Allow to stand several hours or until the blue color has entirely disappeared (the further addition of zinc may be required to bring about this result). What becomes of the zinc and of the copper sulphate? Test the filtrate with ammonium hydroxide (?). Does this indicate the presence of copper ions? Collect the black precipitate in a test-tube and add to it a few drops of nitric acid (?) and finally ammonium hydroxide carefully (?). What can you say of the position of zinc with reference to copper in the electro-motive series (cf. 6 b)?

SILVER.

81. REACTIONS OF SILVER SALTS.

a. Take some silver nitrate solution and add to it dilute hydrochloric acid till no further precipitation occurs. Filter and wash with water.

What effect does the skin have on silver nitrate?

See Chap. VII., 4 g, for solubilities of the silver chloride. Try the action of a concentrated solution of sodium thiosulphate upon a little silver chloride (?).

b. Expose a portion of the precipitate upon a filter paper to the action of direct sunlight (?).

c. Place the rest of the precipitate in a porcelain crucible, put on it a piece of granulated zinc, and fill up with dilute sulphuric acid. Stir from time to time (?). After an hour or two pour off the acid, take out any unchanged zinc, wash the precipitate with water by decantation, add ammonium hydroxide, and filter. Find out whether there is any silver chloride in the filtrate (cf. Chap. VII., 4 g). When the filter paper is dry, place the dark powder in a hollow on a stick of charcoal and melt it with the flame of the blast-lamp directed downward upon it (?).

d. Add a solution of potassium bromide to a few c.c. of a silver nitrate solution. Filter off the precipitate and try its solubility in a concentrated solution of sodium thiosulphate (?). (Recall also the solubilities in Chap. VIII., 4 d. Does light affect silver bromide?

e. Add a solution of potassium iodide to a little silver nitrate solution (?). Filter off the precipitate and try its solubility as in d. (Recall experiment Chap. VIII., 4 d.

Does light affect silver iodide?

How would you rate the solubility of silver chloride, bromide, and iodide in ammonium hydroxide? What complex cation is formed [R. 630]? How does the concentration of the argention in silver iodide compare with that in this complex ion? How does it compare also with that in the complex silver thiosulphate ion?

f. Pass a stream of hydrogen sulphide into a dilute solution of silver nitrate (?). Filter off and wash the precipitate with water. Try the action of dilute nitric acid upon a small portion of it (?). Try the action of ammonium hydroxide upon a second portion (?).

g. Add a few c.c. of a solution of potassium cyanide to a silver nitrate solution (?). What is formed? Continue the gradual addition of the cyanide solution (?). What exists now in the liquid?

Try the effect of adding a little potassium chloride solution to a portion of the liquid (?). What ions are shown to be absent? If absent, and no double salt is therefore present (?), what complex ion shall we find?

Pass a current of hydrogen sulphide into a second portion of the liquid (?). What does the result indicate regarding the concentration of argentions in silver sulphide and in the complex silver cyanide ions [R. 630]? Compare the concentration in these two cases with the concentration of argentions in silver chloride. Will silver chloride (as well as the other halides) dissolve then in a solution of potassium cyanide [R. 630]?

h. To a little silver nitrate solution add some potassium

dichromate solution (?). Test the solutions before and after mixing, with neutral litmus paper (?). [If the color of the dichromate obscures that of the litmus, wash the test-paper with distilled water.]

82. THE PROPERTIES OF A METALLIC ELEMENT.

The properties of a metal, in the chemical sense of the word, are: (1) The element may be the sole constituent of a cation (positive ion). (2) Its hydroxyl compound is a base. (3) Its salts should not be hydrolyzed by water.

Do copper and silver completely fulfil these conditions? If not, in what respects do they fail to do so?

CHAPTER XIX.

MAGNESIUM, ZINC, CADMIUM, MERCURY.

83. PROPERTIES OF MAGNESIUM COMPOUNDS.

a. Try whether magnesium chloride dissolves completely in water (?). Test the solution with litmus (?).

Heat some of the crystals strongly in a dry test-tube (?). Test the reaction towards litmus paper of the water which condenses in the tube (?), and then remove the liquid from the sides of the tube with a piece of filter paper. Does the residue dissolve in water? Explain.

b. To some diluted magnesium sulphate solution add ammonium hydroxide (?). Explain the result in terms of the theory of ionization. Now mix with some ammonium hydroxide several times its volume of ammonium chloride solution (would ammonium sulphate answer as well?) (what effect will this have on the ionization of ammonium hydroxide (cf. 5 b?)) and then add the mixture to a fresh portion of the magnesium sulphate solution (?). Explain. To this combination of three solutions add sodium phosphate solution (?) [R. 645]. Write the equation and explain the purpose for which each ingredient was used.

c. To a diluted solution of magnesium sulphate add a small quantity of sodium or potassium hydroxide and filter (?). Try the solubility of this precipitate (1) in acids (?), (2) in an excess of the reagent (?), (3) in a strong solution of ammonium chloride (relate this action to that in b) (?) and save the filter paper holding a little of the precipitate for f.

d. To a fresh portion of the diluted magnesium sulphate solution add ammonium carbonate solution and warm (?). What other metal ions were precipitated by the same reagent? Repeat, adding excess of ammonium chloride solution to the magnesium sulphate solution before using the carbonate (?). Try whether,

with this modification, the salts of those other metals still behave like those of magnesium. If you had a salt of magnesium mixed with a salt of one of those other metals, how would you proceed so as to precipitate a compound of the alkaline earth metal first and one of magnesium afterwards? Explain the effect of the ammonium chloride as in *b*.

Add two drops of hydrochloric acid (why?) to about 250 c.c. of the city water, evaporate to small bulk, and test it for calcium and magnesium.

e. Pass hydrogen sulphide through some magnesium sulphate solution (?). Explain.

f. Roll up a piece of the filter paper from *c* containing a small quantity of magnesium hydroxide and twist a platinum wire tightly around it. Roast the whole in a Bunsen flame. Remove and moisten the ash with a cobalt chloride solution and roast again (?).

ZINC.

84. PROPERTIES OF ZINC COMPOUNDS.

a. To a diluted solution of zinc sulphate (test the solution with litmus (?)) add an excess of a solution or normal sodium carbonate (?). What gas is evolved in the reaction? Bring the contents of the tube to a boiling point and filter. Try the action of an acid upon a small portion of the precipitate (?). Is it a carbonate? If so, account for the evolution of gas as above. Dry the precipitate and reserve for *b*.

b. Place the dried basic zinc carbonate from *a* in a porcelain crucible and heat to redness for a few minutes. Remove a small portion of the product and try the action of an acid upon it (?). (If an effervescence is perceptible ignite for a longer time). What is the product finally obtained? What is its color hot, and also when cold? Reserve for *c*.

c. Moisten the residue in *b* with a few drops of a cobalt chloride solution and heat again (?). Note the color of the product. By what name is it known [R. 648] ?

d. To a dilute solution of zinc sulphate add a little sodium hydroxide solution (?). What is formed? Divide the contents of the tube into three equal portions. To one add a little dilute hydrochloric acid (?). To the second add an excess of the reagent—sodium hydroxide (?). If the reagents employed are of approximately equal strength, a comparison of the amounts required for solution in both cases may indicate the relative degree of ionization, first as a base and second as an acid [R. 648]. To the third portion add ammonium hydroxide [R. 648] (?). What complex ion is here formed?

e. Relative Activity of Acids. In three clean test-tubes place

(1) zinc chloride, (2) zinc sulphate, and (3) zinc acetate solutions. Test each with litmus paper (?). Pass hydrogen sulphide to saturation (test ?) through each solution (?). Filter the mixtures separately, test the reaction of each filtrate with litmus paper (?), and add ammonium hydroxide to each (?). In considering the nature of the product produced by the last reagent, remember that the water is saturated with hydrogen sulphide, and that therefore ammonium sulphide is formed in it.

How do the three salts differ in behavior? How do you account for this difference? In answering this question it will be found helpful to scrape a little of the precipitate into each of the two test-tubes and to treat one with diluted hydrochloric acid (?) and the other with diluted sulphuric acid (?). What evidence is there that the actions are reversible? Which shows this most markedly and which least so? Can you infer from this the relative activities of the three acids?

f. Ionic Equilibrium. Take a larger amount of zinc sulphate solution and add sulphuric acid to it cautiously until a sample ceases to give any precipitate with hydrogen sulphide. Explain. Now add much powdered solid sodium sulphate, stir until it has dissolved, and test a part with hydrogen sulphide again. Explain. Write this equation so as to show that the action is reversible and that an equilibrium exists.

g. Repeat *f* using sodium acetate in place of sodium sulphate. Do you obtain better results? Explain.

h. To a small quantity of zinc sulphate solution add a solution of ammonium sulphide (?). Is the precipitation complete in this case? Why?

CADMIUM.

85. PROPERTIES OF CADMIUM COMPOUNDS.

a. To a solution of any cadmium salt, e. g., the sulphate (test with litmus paper (?)) add a solution of sodium hydroxide in excess (?). Compare the action here with that of zinc hydroxide (cf. 84 *d*). Try the solubility of cadmium hydroxide (1) in hydrochloric acid (?), (2) in ammonium hydroxide (?) and compare likewise with zinc in this connection [R. 651].

b. Into a second portion of the cadmium sulphate solution pass a stream of hydrogen sulphide (?). Try the solubility of the precipitate (color?) in hydrochloric acid (?) and in alkaline sulphides (?). Compare in these respects with the sulphide of zinc. By what reactions could you distinguish between salts of magnesium, zinc and cadmium?

86. Apply to the instructor for three unknown substances and identify them.

MERCURY.

87. MERCUROUS NITRATE.

Place about 10 g. of mercury with 15 c.c. of diluted (1:1) nitric acid in a small beaker and let the action go on for an hour or two, or until fresh crystals cease to be formed. If crystallization is long in starting, stirring, or infection with a crystal of mercurous nitrate will bring it about. Pour away the liquid and dissolve the crystals in water to which a few drops of nitric acid have been added (why?). This solution, if ready, may be used in 89.

88. MERCURIC NITRATE.

Repeat 87 above, using but a few grams of mercury and boiling the solution till all the mercury is dissolved. Evaporate the solution to dryness over a water-bath, adding a little concentrated nitric acid from time to time.

89. REACTION OF MERCURIC AND MERCUROUS SALTS.

Use diluted portions of mercurous nitrate and of any mercuric solution at hand. Compare the results in each case.

- a. Try the reaction of each solution to litmus (?).
- b. Add dilute hydrochloric acid to each (?). Treat the precipitate, if there is any, with ammonium hydroxide [R. 659] (?).
- c. Add a sodium hydroxide solution [R. 656] (?).
- d. Add ammonium hydroxide [R. 659] (?).
- e. Pass a current of hydrogen sulphide through each to saturation (?), then acidify [R. 657] (?). Try the action of dilute nitric acid upon mercuric sulphide (?).
- f. Add to each a solution of potassium iodide till there is no further change (?). Note the change of color displayed. What is the color of the potassium—mercuric ion? Does mercuric sulphide give a less concentration of mercuric ions than this complex ion? Try an experiment which will show this.
- g. Add a solution of stannous chloride to each till no further change takes place [R. 655] (?).
- h. Drop a few pieces of copper into the solutions (?). Ascertain experimentally whether any copper goes into solution (?). What position will mercury take with reference to copper in the electro-motive series?
- i. Heat any salt of mercury strongly in a narrow tube closed at one end (?).

90. How could you distinguish solutions of mercurous and mercuric salts, respectively, from salts of silver, copper, magnesium, zinc and cadmium?

Do these four metals exhibit the properties of metallic elements (cf. 82)? If not, in what respects do they fail?

91. Apply to the instructor for three unknown substances and identify them.

CHAPTER XX.

ALUMINIUM, TIN, LEAD.

92. ALUMINIUM.

a. Recall the effect of hydrochloric acid on aluminium (Chap. IV, 2 *a*) (?). Try the action of dilute sulphuric acid (?) and also of dilute nitric acid (?) upon the metal.

b. Heat a piece of aluminium wire with sodium hydroxide solution for some minutes (?). What gas is evolved? What gas is evolved? Neutralize a portion of the solution very carefully with dilute hydrochloric acid (?). What is precipitated? To ascertain whether this precipitate is a compound of aluminium the test in 94 *f* may be applied.

c. To the second portion of the solution from *b* add a solution of calcium chloride (?). What is precipitated? Give the generic name for the crystalline products of this type that occur in nature [R. 685] ?

93. ALUM.

Prepare warm ~~saturated~~ solutions of anhydrous aluminium sulphate and potassium sulphate in approximately equimolecular proportions, mix them, and set aside (?). Obtain some large crystals by suspending a thread in the solution. Note the taste and form of the crystals. Reserve for 94 *b*.

94. REACTIONS OF ALUMINIUM COMPOUNDS.

Use a diluted solution of aluminium sulphate.

a. Test the solution with litmus (?).

b. Add a little ammonium hydroxide to the solution (?). What is precipitated? Try the solubility of this precipitate (1) in hydrochloric acid (?), (2) in an excess of ammonium hydroxide (?). Reserve a third portion for *f*. Will a solution of an alum react in a similar manner toward ammonium hydroxide? Try the experiment with a solution made from crystals in 93. Does this show the molecular structure of an alum to be that of a double salt or a salt of a complex acid?

c. Gradually add a solution of sodium hydroxide to a solution of the aluminium sulphate (?). Compare the precipitate with that obtained in *b*. Now add an excess of the sodium hydroxide solution (?). What is formed in this case? What other hydroxide showed similar properties (cf. 84 *d*)? Boil a portion of the solution with some ammonium chloride (?). Relate the action here to that in 92 *b* and account for the precipitation.

d. Add now a solution of ammonium carbonate to a portion of this aluminium sulphate solution (?). Isolate the precipitate and ascertain whether or not it is a carbonate (?). Account for

the reaction of its production. May we expect the same result with an alum? Will sodium carbonate react in a similar way?

e. To another portion of the aluminium sulphate solution add colorless ammonium sulphide (?). Filter off the precipitate and ascertain whether or not it is a sulphide (?) Reserve a part of the precipitate for use in *f*.

f. Place the precipitate from either *b* or *e* in a porcelain crucible and ignite. Cool and add a few drops of cobalt chloride solution and heat again (?). Observe color.

95. MORDANTING.

a. To some cochineal solution add any solution containing a salt of aluminium and then ammonium hydroxide (?). Filter. What becomes of the coloring matter?

b. Now soak a piece of cloth in a strong solution of alum and then transfer it to a beaker containing a boiling solution of cochineal made strongly alkaline with ammonium hydroxide (?). What purpose does the alum serve? What is the object of the ammonium hydroxide? Might a salt of aluminium be selected, which, by hydrolysis would accomplish the same result [R. 688]?

TIN.

96. TIN.

a. Try the action of very dilute nitric acid upon tin. Apply a test to the solution for the presence of ammonium salts (?). If present, account for the same [R. 694].

b. Treat a small granule of tin with hot concentrated nitric acid (?). What difference in result here from that in *a*? Account for this difference. Is the precipitate a pure metastannic acid [R. 694] ?

97. HALIDES OF TIN.

a. Stannous Chloride. Recall the action of hydrochloric acid upon tin (cf. Chap. IV, 2 *a*) (?). Dissolve about 1 g. of tin in warm concentrated hydrochloric acid. Let the action proceed until the acid is nearly exhausted. Use the solution in *b* and 98.

b. Stannic Chloride. Treat the solution from *a* with a few drops of bromine until the color ceases to be destroyed and then drive off the excess of bromine by warming (?). Reserve the solution for 98.

98. REACTIONS OF STANNOUS AND STANNIC SALTS.

Use small portions of each of the solutions from 97 *a*, *b*, after diluting with water.

a. Saturate (test?) a portion of the stannic chloride solution with hydrogen sulphide (?). Filter off the precipitate (color?) and try its solubility (1) in a dilute acid and (2) in a warm colorless ammonium sulphide solution [R. 697] (?). What is the action of dilute hydrochloric acid upon the solution formed in this latter case?

b. Repeat *a* using a little of the stannous chloride solution (?). What is the color of stannous sulphide? If it does not dissolve in the colorless ammonium sulphide solution add a pinch of sulphur and warm (?). Explain the action here. To prove this add hydrochloric acid, observe the precipitate, and compare with that formed in *a*.

c. Add a little mercuric chloride solution to a few c.c. of the stannic chloride solution (?). Now add the mercuric chloride solution to a little of the stannous chloride solution and observe the two changes (?). When the precipitation is complete (?) filter off the precipitate (?) and add to the filtrate a little of the mercuric chloride solution (?). What does this show in regard to the change the stannous chloride has undergone?

Boil a portion of the stannic chloride solution with a granule of tin for a few minutes. Now try the action of mercuric chloride upon a little of this solution (?). Account for the loss in the electric charge of the stannic ions?

d. Add a little sodium hydroxide solution to portions of the stannic and stannous chloride solutions (?). Filter off the precipitates [R. 696] and try their solubility (1) in hydrochloric acid (?), (2) in an excess of sodium hydroxide (?). Compare in these respects with aluminium hydroxide.

99. EQUIVALENT WEIGHT OF TIN [Hood].

Place about 5 g. of tin in a porcelain crucible, pour upon it 5—10 c.c. of conc. nitric acid and heat over a sand-bath. When the tin is entirely consumed evaporate off all the acid and ignite the residue over a Bunsen burner. Cool and weigh. Calculate the equivalent weight of tin in the compound, assuming that of oxygen to be 8. The atomic weight of tin is 119, what is the formula of the compound?

LEAD.

100. LEAD.

a. Dissolve 1 g. of lead acetate in 20 c.c. of water, place in it several pieces of granulated zinc and let them remain for an hour or two. Preserve the solution and, after 102, devise a way of precipitating any remaining ionic lead and showing the presence of zinc in the solution, and see whether it works.

b. Wash some of the lead from *a* with distilled water and see whether it is possible to get washings which show no reaction with hydrogen sulphide (?). Account for what you observe.

c. Strongly heat a mixture of any lead salt with equal parts by weight of sodium carbonate (anhydrous) and powdered charcoal, in a porcelain crucible. Cool, wash with water and examine the residue (?). Heat this product separately in the crucible, stirring with a file (?). What is produced [R. 700]?

101. LEAD NITRATE.

Dissolve, by gentle warming, about 2 g. of litharge with dilute nitric acid in a test-tube. Filter and evaporate the clear solution over a water-bath (Hood) to the point of crystallization. Reserve the crystals for 102. May this salt also be prepared by the action of nitric acid upon lead?

102. REACTIONS OF LEAD SALTS.

Use a diluted solution of lead nitrate, or the salt prepared in 101.

- a. Test the solution with litmus (?).
- b. Add sodium hydroxide gradually (?) and then in excess (?). Compare the behavior of the hydroxide with that of hydroxides of zinc, aluminium and tin.
- c. Try the action of hydrogen sulphide (?) Is lead sulphide soluble (1) in hydrochloric acid (?), (2) in dilute nitric acid (?).
- d. Add hydrochloric acid to a portion of the solution (?). Filter, dilute the filtrate, and pass hydrogen sulphide through it (?). Explain. What other chlorides are more or less soluble in water?
- e. Add a solution of potassium iodide to another portion (?). Boil the contents of the tube, filter, and examine the filtrate (?). What property of plumbic iodide is indicated (cf. Chap. VIII, 8 d)?
- f. Add a potassium dichromate solution to a portion of the solution (?). Test the solutions with litmus paper before and after mixing (?). The result will throw light on the nature of the reaction.

Does lead form any compounds in which it is quadrivalent [R. 698] ?

103. LEAD DIOXIDE.

Place 1 g. of red lead (minium) in a test-tube and add 5—6 c.c. of dilute nitric acid. Warm gently until the red color of the substance is no longer discernible. The brown powder now remaining is lead dioxide. Dilute with water and pour off the clear liquid into another tube. Apply the tests in 102 c, e to prove the presence of lead in this liquid (?). In the action of the acid what is indicated regarding the probable structure of red lead [R. 701] ?

104. Do these metals exhibit the properties of metallic elements? If not, in what respects do they fail?

105. Apply to the instructor for three unknown substances and identify them.

CHAPTER XXI.

ARSENIC, ANTIMONY, BISMUTH.

106. ARSENIC [Hood].

- a. Heat a very small particle of arsenic in a hard glass test-tube. Notice its behavior (?).
- b. Heat also a very small particle of arsenic in a crucible lid (?). Of what does the vapor consist? Note the odor.
- c. Mix a pinch of powdered arsenic trioxide with an equal amount of powdered wood charcoal. Place the mixture in a test-tube, cover it with a little more wood charcoal and heat strongly (?). Compare the sublimate with that obtained in a.
- d. Boil a pinch of powdered arsenic with an excess of nitric acid (?). What evidence is there of action (cf. 36 a)? Reserve the solution for examination under 109 f.

OXYGEN COMPOUNDS OF ARSENIC.

107. ARSENIOS OXIDE AND ARSENIOS ACID.

- a. Boil a pinch of arsenic trioxide with about 5 c.c. of water in a test-tube. Is the trioxide very soluble? Test the solution with litmus paper (?). Now add a few c.c. of sodium hydroxide solution to the test-tube and boil again (?). To what class of oxides does the trioxide appear to belong?
- b. Boil a pinch of the trioxide with a little conc. hydrochloric acid (?). To what class of oxides does the trioxide now appear to belong? Remove a small portion of the liquid and allow to stand (?) What are the crystals? Dilute the remainder of the solution with water and reserve for 110.

108. ARSENITES.

- a. To a solution of potassium arsenite add a little silver nitrate solution (?). Divide the mixture into two portions; into one pour an excess of ammonium hydroxide (?) and into the other an excess of nitric acid (?).
- b. Add a drop or two of a copper sulphate solution to a little of the potassium arsenite solution (?). What is the precipitate [R. 712]?
- c. Pass a current of hydrogen sulphide into a solution of potassium arsenite and observe result (?). Try the effect of adding a little conc. hydrochloric acid to the solution during the operation (?). Filter off the precipitate (?) and try its solubility (1) in conc. hydrochloric acid, (2) in colorless ammonium sulphide solution (?). What occurs when its solution in ammonium sulphide is acidulated with hydrochloric acid (cf. 98) [R. 694]?

109. ARSENIC ACID AND ARSENIATES.

- a. Boil a pinch of arsenic trioxide with a little nitric acid in

a test-tube until brown fumes cease to be evolved (?). Evaporate the solution to dryness over a water-bath [Hood] and dissolve the white residue (?) in warm water (15—20 c.c.).

b. To a portion of this acid solution from *a* add a few drops of silver nitrate solution (?). Now neutralize the mixture with a very little ammonium hydroxide (?) and divide it into two portions. To one of these add an excess of ammonium hydroxide (?), to the other an excess of nitric acid (?).

c. To a second portion of the acid solution from *a* add a little "magnesia mixture" (?). Relate this to the action of phosphates (cf. 37 c).

d. To a third portion of the solution from *a* add an excess of a solution of ammonium molybdate in nitric acid [Side-shelf] and apply a gentle heat (?). Relate this also to the similar reaction of phosphates (cf. 36 b).

e. Pass a current of hydrogen sulphide into another portion of the arsenic acid solution above (?). Acidify strongly with conc. hydrochloric acid and again pass in the current of the gas (?). Heating the solution will facilitate the reaction. Explain.

f. Test the solution from 106 *d* (after the greater part of the nitric acid has been driven off [Hood]) with an excess of the ammonium molybdate solution as described in *e* (?). What acid is thus identified? Compare arsenic with phosphorus in this respect.

ARSENIC AND HYDROGEN.

110. ARSINE [Hood. *Care! Poison!*] (In presence of instructor.)

Arrange a small flask with safety and delivery tubes and nozzle to generate and burn hydrogen. Place in it a piece of chemically pure zinc and add pure hydrochloric acid. When the air has been displaced [*Care! Test?*], light the gas by means of a tube of burning hydrogen (cf. Chap. IV, 3), and hold a crucible lid in the flame (?). If there is no deposit, add a drop or so of the solution of arsenic trichloride (107 *b*), observe the appearance of the flame, and obtain a deposit on the crucible lid (?). What kind of chemical change takes place in the flame (cf. 8 *c*)? Heat the tube through which the gas passes to the nozzle, with a Bunsen flame (?) (Marsh's test). When these experiments are completed, fill the test-tube with water to stop the action.

Describe the appearance of the deposit (?).

Apply fresh bleaching powder solution to the deposit on the crucible lid by means of a glass rod (?).

What way of making arsine is identical in principle with that used for phosphine in 34 [R. 709] ?

How do ammonia and phosphine behave when heated [R. 461] ?

ANTIMONY.

111. ANTIMONY.

- a, b.* Try the same with antimony as with arsenic, 106, *a, b.*
c. Same as 106, *c*, substituting antimonious oxide for arsenious oxide (?).

OXYGEN COMPOUNDS OF ANTIMONY.

112. ANTIMONIOUS OXIDE.

a. Heat a pinch of powdered antimony with conc. nitric acid until the antimony is converted into a white product (?). How could you ascertain whether this product was a nitrate or not? In what way does the action of nitric acid upon antimony differ from its action upon arsenic (106 *d*)? Dilute the contents of the tube with water, filter and wash the product well with water while on the filter. Reserve for *b*.

b. Place the antimonious oxide from *a* in a test-tube and, after washing several times with water by decantation, boil it up with a little water (?). Is it soluble? Is its solution acid to litmus? Now add sodium hydroxide solution and boil again (?). What kind of an oxide does this show it to be?

c. Boil a pinch of antimonious oxide [Side-shelf] with 5—6 c.c. of conc. hydrochloric acid in a test-tube (?). What kind of an oxide does this show the trioxide to be? Evaporate this solution to a small bulk and note the formation of heavy white fumes (?).

d. Boil about 1 g. of antimony trioxide with the same amount of potassium acid tartrate (common name?) dissolved in 10—12 c.c. of water (?). Filter the solution and set the filtrate aside (?). What are the crystals [R. 716] ?

113. ANTIMONIC ACID AND ANTIMONIC OXIDE.

a. Heat about 1 g. of antimony trioxide with conc. nitric acid in a test-tube (?). Is there any evidence of action? Pour the mixture into a crucible and evaporate it to dryness, finally heating to a little below a red heat (?). What is the color of the product formed [R. 715] ? Might some of this substance have been formed in 112 *a*? Reserve for *b* and *c*.

b. Boil a small portion of the product from *a* with water (?). Is it soluble? Try the action of a sodium hydroxide solution upon a portion of it (?). What kind of an oxide does it appear to be?

c. Heat the remaining portion of the product from *a* to redness in a crucible. Cool and observe the color (?). Try its solubility (1) in hydrochloric acid (?), (2) in sodium hydroxide (?). What kind of an oxide is it [R. 715] ?

114. REACTIONS OF ANTIMONIOUS COMPOUNDS.

a. Dissolve a small amount of antimony trichloride in water and test the solution with litmus paper (?). Add more water,

warm, and make a clear solution by adding small quantities of concentrated hydrochloric acid (?), agitating vigorously after each addition. Reserve for *b* and *c*.

b. To half of the solution from *a* add a large amount of water [R. 715] (?). What kind of action is this? Add concentrated hydrochloric acid again (?). How does this illustrate the influence on a reversible action of change in concentration of one factor? Write the equation which combines both actions.

How could you show that the molecules of the trichloride are only partly hydrolyzed by water, leaving a basic salt (with phosphorus trichloride the hydrolysis was complete)? What is the significance of this difference [R. 719] ?

c. Through the remaining half of the trichloride solution from *a* pass a current of hydrogen sulphide to saturation (test?) (?). Filter off the precipitate and try its solubility in a hot yellow ammonium sulphide solution [R. 717] (?). What takes place upon the acidification of its solution in the latter with hydrochloric acid?

115. STIBINE.

Follow all the directions in 110, using a solution of antimony trichloride in place of that of arsenic trichloride.

BISMUTH.

116. BISMUTH.

Prepare a match or pine splinter as in 79 *e*. Place on the end of it a mixture of any bismuth salt with anhydrous sodium carbonate, heat in the reducing region of a Bunsen flame, break up with water in a mortar and examine the residue (?).

117. BISMUTH COMPOUNDS.

a. Dissolve, by gentle warming, about 1 g. of bismuth in 8—10 c.c. of nitric acid diluted with an equal volume of water. Evaporate the solution to one-third its volume and allow to stand (?). Examine the crystals.

b. Dissolve about 1 g. of bismuth nitrate, or the crystals from *a*, in a little water by the addition of the least possible amount of nitric acid. Pour a part of this solution into a large amount of water (100 times its own volume) (?). Try the effect of adding a little nitric acid to the tube (?). Write the equation to show that an equilibrium exists.

c. Pass a current of hydrogen sulphide into the second portion of the solution of bismuth nitrate from *b* (?). Filter off the precipitate. Try its solubility (1) in hydrochloric acid (?), (2) in nitric acid (?), (3) in ammonium sulphide solution (?). Compare in these respects with the sulphides of arsenic and antimony (?).

d. Add sodium hydroxide solution to a small quantity of a bismuth salt solution (?). Relate this property to those of arsenic and antimony toward the same reagent. Filter off the precipitate and ignite it in a porcelain crucible (?). Note the color of the product both hot (?) and cold (?).

118. Apply to the instructor for two unknown substances and identify them.

CHAPTER XXII.

CHROMIUM, MANGANESE.

119. CHROMIC OXIDE.

Mix some potassium dichromate (15 g.) thoroughly with one-fifth its weight of powdered sulphur and heat with the blast-lamp in a porcelain crucible for fifteen minutes. Grind up the resulting mass in a mortar with water, filter, wash the green residue (?), and dry it on a radiator for use in 120.

Make a borax bed, dissolve a particle of chromic oxide in it, and note the effects of oxidizing and reducing flames on it (?). All chromium compounds give the same result. If chromic sulphate had been used, what would have been the nature of the chemical action?

120. CHROMIC CHLORIDE.

Mix the chromic oxide prepared in 119 with one-third its weight of powdered wood charcoal, make into a stiff paste with some starch, and mold the mixture into little pellets of the size of peas. Cover these completely with a layer of charcoal powder (why?) in a closed crucible, dry them by heating with the Bunsen flame and let them cool before exposing them to the air (why?). Place them in a piece of hard glass tubing. Then connect with a chlorine apparatus and, when the chlorine gas has reached the pellets and completely displaced the air (why?), heat strongly with a blast-lamp. Conduct any superfluous chlorine into a test-tube filled with sodium hydroxide. Describe the substance which is formed and try its solubility in water and acids.

121. CHROME-ALUM.

Dissolve 10 g. potassium dichromate in water, add the amount (calculated) of sulphuric acid necessary to form potassium sulphate and chromium sulphate, warm and add alcohol (7—10 c.c.), a little at a time, until the yellow color has entirely given place to a pure, bright green. The action takes some time to reach completion. Notice the odor (?). Set the greater part of the solution aside to evaporate spontaneously. Concentrate the smaller portion over a water-bath till crystals appear. Examine

the form and color of the two sets of crystals (?). What is the color of their solution in water? Ascertain by this dilution the color of the trichromion (?).

122. CHROMATES.

Melt 5 g. of potassium carbonate with equal amounts of potassium hydroxide and potassium nitrate at a low temperature in an iron crucible and stir in (use the reverse end of a file) 5 g. of powdered chromite. Heat strongly [Blast-lamp] for several minutes (?). When the mass has cooled dissolve it in a little boiling water. Add dilute nitric acid until the solution is acid (?). Note the change in color (?).

123. CHROMIUM TRIOXIDE.

Make a cold saturated solution of 5 g. of sodium dichromate, add it to two volumes of concentrated sulphuric acid and cool (?). Filter through a small plug of asbestos and dry the precipitate by spreading it on a piece of broken bisque plate [Store-room].

124. DICHROMATES AND CHROMATES.

a. Take some potassium dichromate solution and run into it potassium hydroxide solution from a burette till the change in color is complete. A test-tube trial will show the tint to be reached. Concentrate the solution and allow it to crystallize (?). What kind of salt (neutral, acid, basic, double, or complex) is potassium dichromate essentially? What is the color of the dichromanion?

b. Dissolve about 2 g. of potassium chromate in 10—12 c.c. of water and add dilute sulphuric acid drop by drop until the change in color is complete (?). Concentrate the solution and set aside. What salt crystallizes out?

125. REACTIONS OF CHROMIC SALTS.

Use diluted, freshly prepared chrome-alum solution. What are the ions in the solution?

a. Boil one portion of the solution for some time [R. 730] ? What was the original color of the solution?

b. To another portion add sodium hydroxide solution, at first a little (?), then excess (?). Boil. [R. 729].

c. Add colorless ammonium sulphide (?). Is the precipitate a sulphide? Filter off the precipitate, wash it with water and apply the test for sulphides (?).

d. Add excess of sodium hydroxide solution and then a large volume of bromine water, and heat (?). Try another portion using lead dioxide instead of bromine (?) Infer the nature of the action from the change in color.

126. REACTIONS OF CHROMATES.

Use diluted potassium chromate solution. What are the ions in the solution?

a. Acidify the solution with dilute nitric acid (?).

b. Recall the actions of hydrogen sulphide, of sulphur dioxide, and of hydrogen peroxide, on such an acid solution (?).

c. Add colorless ammonium sulphide, heat and maintain at the boiling point, noting two distinct changes (?), then acidify (?).

d. Add lead nitrate and barium chloride to separate portions.

e. Add lead nitrate and barium chloride to separate portions of a potassium dichromate solution (?). Compare results with those in *d* and explain.

127. PERCHROMIC ACID.

Dissolve a crystal of chromium trioxide in 10—15 c.c. of water in a test-tube, add a few c.c. of ether and then a little hydrogen peroxide solution. Shake well and observe the color in the ether (?).

128. MANGANESE.

Examine a solution of a manganous salt (e. g., the chloride) and one of potassium permanganate. Add a few drops of a sodium carbonate solution to portions of each (?). Explain the difference in results. Ascertain the color of the manganion and permanganion by diluting separate portions of the solutions above.

129. MANGANATIS AND PERMANGANATES.

a. Fuse a mixture of 5 g. of potassium hydroxide, 2.5 g. potassium chlorate, and 5 g. finely powdered manganese dioxide at a red heat, stirring with the reverse end of a file, until effervescence ceases (?). Add the last ingredient gradually. Treat the mass with a small amount of cold water, decant the clear liquid away from the precipitate, and use it in *b*, *c*, and *d*.

b. Dilute a part of the clear green solution, with a very large amount of water in a beaker (?). If no change should occur, pass carbon dioxide into the diluted solution (?).

c. To a portion of the green solution add a few drops of alcohol and warm (?).

d. To the rest of the green solution add a boiling solution of oxalic acid (?).

e. Repeat *c* and *d* with potassium permanganate solution, acidified by adding two or three times its volume of dilute sulphuric acid (?).

f. Recall the action of hydrogen sulphide (cf. 9 *e*) and of sulphur dioxide (16 *h*) upon an acidified potassium permanganate solution?

130. REACTIONS OF MANGANOUS SALTS.

Use a solution of any manganous salt.

a. Borax bead in oxidizing (?) and reducing (?) flames.

b. Bead of a mixture of sodium carbonate and sodium nitrate on a platinum wire with any manganese compound (?).

c. To a diluted solution of a manganous salt, add ammonium sulphide (?). Is the product a sulphide?

d. To another portion add sodium hydroxide (?). Divide into two parts. Shake one with air (?). To the other add bromine water and warm (?).

131. Apply to the instructor for two unknown substances and identify them.

CHAPTER XXIII.

IRON, COBALT, NICKEL.

132. IRON.

Recall the action of iron on dilute acids (Chap. IV., 2 a, e), also its conversion into the oxide by decomposition of the nitrate (cf. Chap. VI., 3 a) and the reduction of an oxide to the metal (cf. Chap. IV., 5).

133. FERRIC SULPHATE AND FERRIC AMMONIUM SULPHATE (Iron Alum).

a. Weigh 3.5 g. of concentrated sulphuric acid into an evaporating dish, add 20 g. of crystallized ferrous sulphate, and dissolve in 25—30 c.c. of water. Heat on a square of wire gauze [Hood] and add concentrated nitric acid drop by drop till the color of the solution, dark at first (?), changes to a light brown. Evaporate to a syrup on the water-bath, dissolve the residue in the minimum amount of boiling water, add 3.5 g. of ammonium sulphate, likewise dissolved in the minimum amount of boiling water, and set aside to crystallize. Describe the crystals (?). Collect them and wash them free from the mother liquor, dry with filter paper, and preserve for use in 135.

Chlorine, bromine and other oxidizing agents have the same effect as the nitric acid here used. With what other have we previously produced the same change?

b. Dissolve some ferric sulphate in water. Note the color (?) and reaction of the solution (?). Add some pure sulphuric acid (?). Account for what you observe and explain the behavior of the salt in terms of the ionic theory.

134. SALTS OF COMPLEX ACIDS.

Ferrocyanide and ferricyanide of potassium. Take some ferrocyanide solution in a test-tube and add bromine water until a drop of the solution gives no blue precipitate with a dilute ferric chloride solution. What does the solution contain [R. 757]?

135. REACTIONS OF FERROUS AND FERRIC SALTS.

a. Make a borax bead with any compound of iron (the oxide or sulphate is best) and examine in oxidizing and reducing flames (?).

For the following reactions use a diluted solution (freshly prepared) of ferrous ammonium sulphate and a diluted solution of iron alum or ferric chloride.

b. Test the action of each solution on litmus paper (?). Which has the stronger effect? What do we infer (cf. 82) from this? If the difference is not well marked try a more sensitive indicator as "congo red" paper.

c. To a portion of each solution add ammonium hydroxide (?). Note the effect on each precipitate of shaking with air (?).

d. Add potassium ferrocyanide solution to portions of each (?).

e. Add potassium ferricyanide solution to portions of each (?).

g. Add a few drops of potassium sulphocyanide (thiocyanate) to portions of each (?).

h. Similarly to portions of each add colorless ammonium sulphide solution (?). Is the precipitate soluble in hydrochloric acid [R. 754]? How could you prove experimentally that free sulphur is formed in the case of ferric salts?

i. Ascertain experimentally whether solutions of ferro- and ferricyanides contain a detectable proportion of iron ions.

136. TRIFERRION AND DIFERRION.

a. What are the colors of these ions? Account for the brown tinge of solutions containing triferriions [R. 755].

b. Boil a few c.c. of a diluted ferric chloride solution with a pinch of powdered iron and test the clear solution according to 135 *c*, *d* and *e* (?). What ions are thus identified?

c. Pass a current of hydrogen sulphide through a solution of ferrous ammonium sulphate (?). Now add a little ammonium hydroxide solution (?). What effect has this latter upon the hydriions? What is the substance precipitated (cf. 135 *h*)? Identify it by proper tests for a sulphide. If a sulphide, what can you say of the relative concentration of diferrion in the sulphide as compared with that in the hydroxide?

d. Pass a current of hydrogen sulphide through a solution of ferric chloride (?). What is the substance precipitated? What is present in the solution? Confirm by applying a suitable test (cf. 135 *g*). Account for the loss in positive charge of the triferriion. Add a little ammonium hydroxide to the solution and compare the result with that in *c* (?).

e. Add an acidified solution of potassium permanganate to a little of the diluted solution of ferrous ammonium sulphate till the pink color is permanent (?). What iron ions are now present in the solution? Confirm by applying a suitable test (See 135 *d*). Compare the result here with that in 133. What change has the diferrion undergone? What change in the permanganion [R. 743] (cf. 129 *e*)?